ABSTRACT

Title of Document: FIELD EVALUATION OF ENHANCED PHOSPHORUS AND NITROGEN REMOVAL IN STORMWATER CONTROL MEASURES.

Jiayu Liu, Doctor of Philosophy, 2014

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This project evaluates two innovative stormwater control measures (SCMs) installed on the University of Maryland campus in College Park, Maryland. One project retrofitted an existing bioretention cell with 5% (by mass) aluminum-based water treatment residual (Al-WTR) to enhance phosphorus removal (P1 site). The other combined a porous parking area with underground anoxic vaults to promote nitrogen removal (N1 site).

At the P1 site, the net reduction of the total runoff was 40% and the volume reduction ratios (f_v) were lower than before the retrofit. The total suspended solids (TSS), total phosphorus (TP), and particulate phosphorus (PP) concentrations were significantly reduced by the bioretention cell, due to the filtration of the particulate matter, while TP export occurred before WTR retrofit. Soluble reactive phosphorus (SRP) and dissolved organic phosphorus (DOP) concentrations in the stormwater

runoff were not obviously changed compared to the system effluent. The near constant outflow of SRP and DOP concentrations suggest an equilibrium adsorption treatment mechanism. Mass loads were reduced for TSS and all P species. WTR incorporation decreased the bioretention media phosphorus saturation index (PSI) from approximately 0.075 to approximately 0.041, which stayed relatively constant during the two year study period, even with the media P continually increasing, indicating a significant increase in media P sorption capacity.

At the N1 site, the flow management achieved nearly zero runoff discharge due to infiltration from the vaults during dry weather. With regard to the porous pavement, approximately 34% of the total nitrogen (TN) (4.7 kg/ha-yr) was mitigated by filtration processes; 6.5 kg/ha-yr particulate organic nitrogen (PON) and 1.8 kg/ha-yr ammonium nitrogen (NH_4^+) were removed, and 4.0 kg/ha-yr oxidized nitrogen (NO_x) were created. In the denitrification vaults, approximately 26% of the TN (3.7 kg/ha-yr) was decreased by system reaction, mostly due to the decrease in NO_x (3.8 kg/ha-yr). PON was reduced slightly, by 0.2 kg/ha-yr. The small amount of DON and NH_4^+ produced likely resulted from leaching from the wood logs. As a result, the N mass reduction that occurred was not only due to volume reduction, but also to system reactions (60%).

FIELD EVALUATION OF ENHANCED PHOSPHORUS AND NITROGEN REMOVAL IN STORMWATER CONTROL MEASURES

By

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Dedication

To my husband, Tong, for his love and support.

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Chapter 1: Introduction

1.1 Background

Bioretention is an EPA-designated low-impact development (LID) best management practice (BMP) for urban stormwater. A bioretention system, as shown in Figure 1-1, usually consists of surface vegetation, a mulch layer, and porous soil media designed to a size of approximately 4% to 5% of the runoff drainage area (Maryland 2007). During rainfall events, runoff goes into the facility instead of being discharged to the surface water directly; excess runoff is held temporarily on the ponding surface once the intensity of rainfall exceeds the media infiltration capacity. As a result, bioretention can mitigate pollutant release, increase groundwater infiltration, and improve water quality.

Phosphorus (P) and nitrogen (N) are nutrients essential for plant growth. Excessive input to water bodies is a common cause of N saturation, eutrophication, and algal blooms in surface water, all of which can lead to poor water quality and a loss of biodiversity in the aquatic ecosystem, and may even cause adverse health effects in humans by contaminating drinking water (Stumm and Morgan 1996; Collins et al. 2010; Ergas et al. 2010). A major source of excess nutrients in surface water is urban stormwater runoff (Bratieres et al. 2008), with sources that include fertilizers, animal wastes, living and decaying plants, detergents, automobile exhaust and atmospheric deposition (USEPA 1999; Davis et al. 2006; Collins et al. 2010).

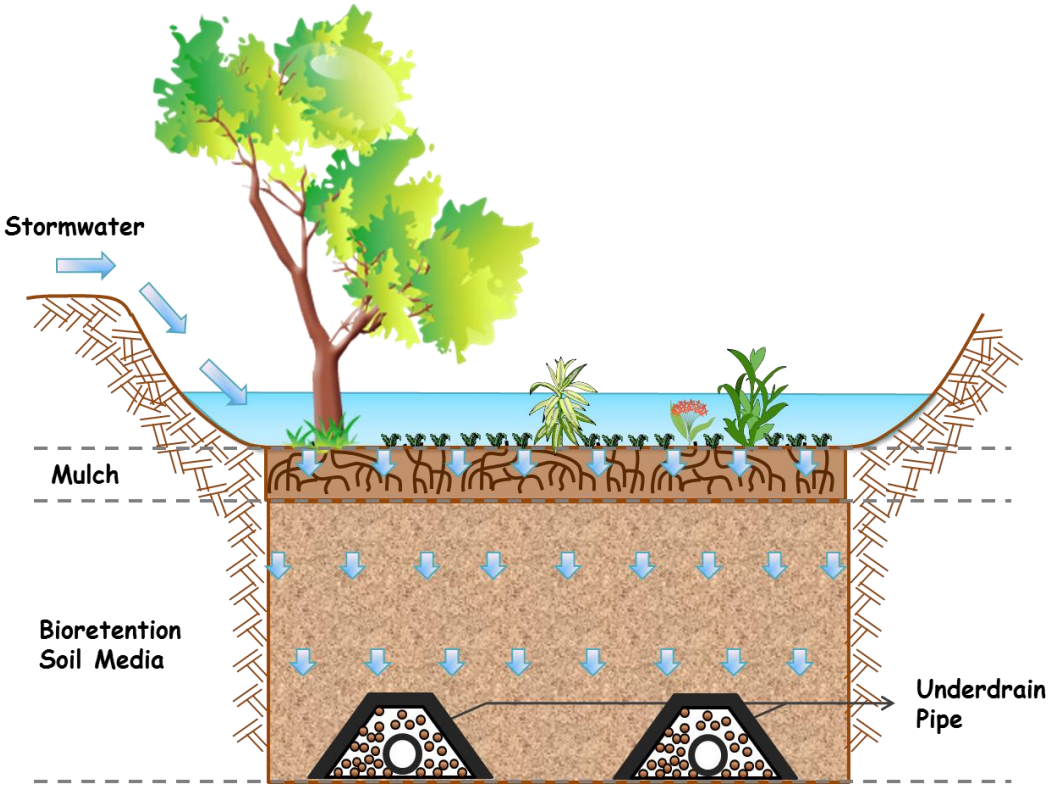


Figure 1-1 Traditional bioretention system.

Bioretention facilities have been proven to successfully manage both flow and volume, as well as mitigate a suite of pollutants, including: suspended solids, hydrocarbons, and heavy metals (Davis et al. 2001; Seby et al. 2001; Davis 2007; Bratieres et al. 2008; Li and Davis 2008a; Li and Davis 2009; Trowsdale and Simcock 2011). The pollutant removal mechanisms include filtration, adsorption, ion exchange, precipitation and biodegradation. However, since nutrient removal is complicated by possible leaching from the media and vegetation within various stormwater control measures (SCM) (Davis et al. 2009), the removal efficiency is highly variable, and the pollutant load reduction commonly results primarily from volume reduction (Li and Davis 2009). Davis's research group has completed both laboratory experiments and field research on nutrient removal. Box experiments have

shown that the removal efficiency of total phosphorus (TP) and total Kjeldahl nitrogen (TKN) were 70% to 85% and 55% to 65%, respectively (Davis et al. 2006). However, field research found that both TP and total nitrogen (TN) concentrations in effluents were higher than in influents (Li and Davis 2009).

Two rain gardens in Connecticut were monitored for a period of 12 months. The TP concentration increased in the effluent, as compared to influent. TKN mass removal was 32%, and ammonia-nitrogen (NH_4^+) mass removal was 85% (Dietz and Clausen 2005a). Hsieh and Davis (2005) found the removal efficiency of TP, nitrate (NO_3^-) and NH_4^+ were 4 – 99%, 1 – 43% and 2 – 49%, respectively in study of eighteen bioretention columns and six existing bioretention facilities. Field research by Hunt et al. (2006) in North Carolina found 40% TN mass removal in conventionally drained bioretention cells, which was due to a substantial volume reduction. However, TP mass removal was 65% in one cell and -240% in the other. Hatt et al. (2009) evaluated the pollutant removal performance of three separate stormwater bioretention systems. Phosphorus concentrations were effectively reduced in two of them, however the third one had elevated phosphorus concentrations in outflow compared to inflow. Moreover, nitrogen concentrations were variable at all sites.

Since traditional bioretention systems may not be effective at removing nutrients from urban stormwater, novel technologies or modifications of traditional methods are needed to provide for enhanced nutrient removal. Some research has indicated that both N and P treatment can be enhanced greatly through modifications

such as adding aluminum- (*Al*-) or iron- (*Fe*-) based materials for P removal, and anoxic storage zone installation for N removal; these reductions potentially can exceed 90% (Lombi et al. 2010; Lucas and Greenway 2011; O'Neill and Davis 2011b; O'Neill and Davis 2011a). However, performance information for field research is sparse. These technologies represent only simple modifications of traditional bioretention cells, and yet they show promising potential for both stormwater volume and nutrient load reduction.

1.2 Enhanced Nutrients Removal

1.2.1 Enhanced Phosphorus Removal

The TP transported by stormwater runoff is comprised of particulate phosphorus (PP) and dissolved phosphorus (DP). Since traditional bioretention relies on physical removal mechanisms such as sedimentation and filtration, bioretention is highly effective at removing PP, but is less successful at addressing DP. The effectiveness of the overall treatment is further complicated by the fact that P partitioning between the particulate and dissolved phases is variable and depends upon site-specific conditions, with the particulate fraction ranging from 20% to > 90% of the total load (Cooke and Bruland 1987; Henderson 2008).

DP removal in bioretention depends upon chemical phosphorus sorption, complexation mechanisms employed to immobilize P species, and the geometry of the flow system (Davis et al. 2001). Retention mechanisms of phosphorus can be thought of as being a combination of a fast reversible true sorption process on soil particle surfaces, plus various slower time-dependent processes, some of which lead

to deposition of P at a depth below the surface of particles (Roy-Poirier et al. 2010). These slower processes can be further subdivided into relatively faster and very slow components, which include the deposition of phosphorus within iron and aluminum oxide mineral structures and precipitation of calcium phosphates. After being retained, inorganic phosphorus is typically considered bioavailable and can be used as a nutrient for plant growth in bioretention facilities, which possibly would allow a removal pathway via harvesting the vegetation (Davis et al. 2006). Hsieh et al. (2007a) investigated the phosphorus removal efficiency in repetitive bioretention columns. They found that long-term phosphorus reactions regenerate active short-term sorption sites. Most of the retained phosphorus in the media layers is available for vegetative uptake and that environmental risk thresholds were not exceeded.

Novel technologies are necessary to accomplish enhanced P removal. Sands with a high metal content (calcium, aluminum, or iron) demonstrated much higher phosphorus-removal capacity than those with lower concentrations of these metals (Arias et al. 2001). The amendment of soil with *Fe* – or *Al* – based water treatment residuals (WTRs), which are byproducts of the coagulation process in drinking water treatment, is one suggested way to mitigate P being leached from agriculture soils with a limited P sorption capacity (Gallimore et al. 1999; Dayton et al. 2003; Novak and Watts 2005; Agyin-Birikorang et al. 2009). Gallimore et al. (1999) applied WTR (collect from AB Jewell reservoir, OK) to plots that received poultry litter in a field scale, mean concentrations of DP concentrations were reduced from 15.0 mg/L to 8.60 mg/L by the litter application of 44.8 Mg ha^{-1}. WTRs that have been co-applied with manures and biosolids can mitigate excess P loss from the soil to the surface

water or groundwater (Agyin-Birikorang et al. 2009). P adsorption occurs at WTR-hydrous iron/aluminum oxide interfaces; phosphate (PO_4-P) replaces hydroxyl (OH^-) groups or water molecules (H_2O) and then reorganizes into a very stable binuclear bridge through mono ligand and/or bidentate ligand exchange mechanisms (Figure 1-2) (Bohn et al. 1985).

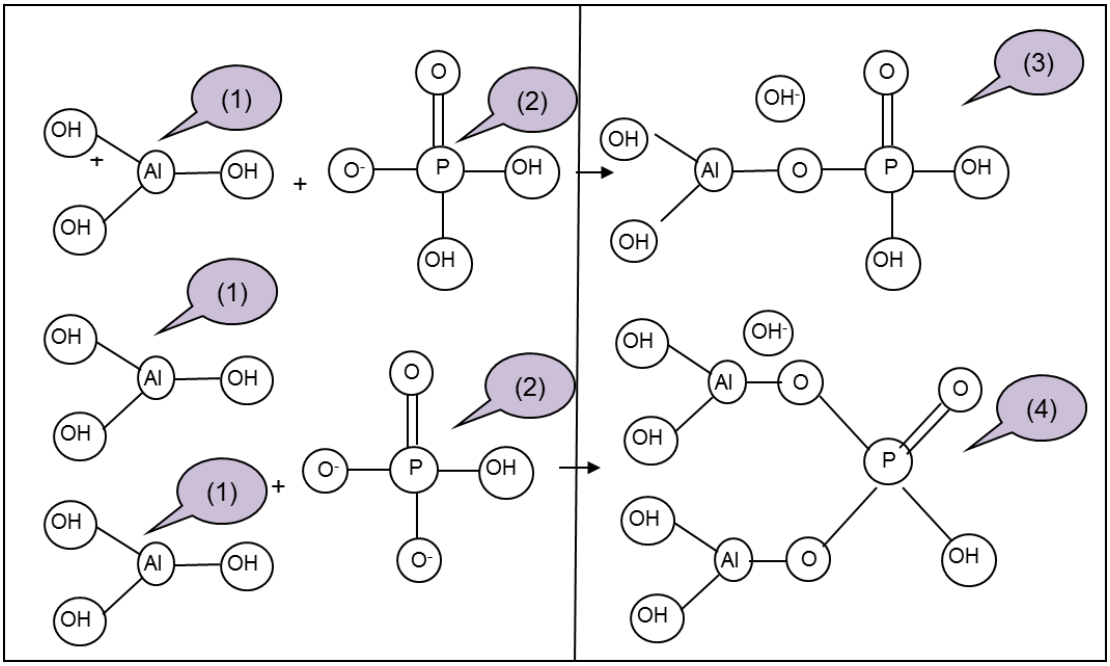


Figure 1-2 Surface reaction of phosphorus chemisorption on WTR. (1) WTR-hydrous aluminum oxide; (2) Phosphate; (3) monodentate ligand; (4) bidentate ligand (Bohn et al. 1985).

Both pilot and laboratory studies have demonstrated that WTR incorporation can greatly enhance P bioretention treatments. In one study (Lucas and Greenway 2011), after the equivalent of over three decades of urban runoff loads, PO_4-P retention ranged from 95% to 99% of the input load, whereas traditional bioretention systems with sandy media appeared to be ineffective for even a decade of urban runoff loads. O'Neill and Davis' (2012a, 2012b) bench-scale and large column research indicated that P treatment can be hugely enhanced through WTR

incorporation. With an input of 0.12 mg/L DP, discharges from a 5% WTR bioretention media column were less than 0.01 mg/L (O'Neill and Davis 2012b; O'Neill and Davis 2012a). Nonetheless, enhanced P performance information for field research is sparse.

1.2.2 Enhanced Nitrogen Removal

Nitrogen in water can be present in a variety of forms depending on the water's pH and redox characteristics, including NH_4^+, nitrate-nitrogen (NO_3^-), nitrite-nitrogen (NO_2^-), dissolved organic N (DON), and particulate organic N (PON) (Li and Davis 2014). Nitrogen transformation processes are shown in Figure 1-3.

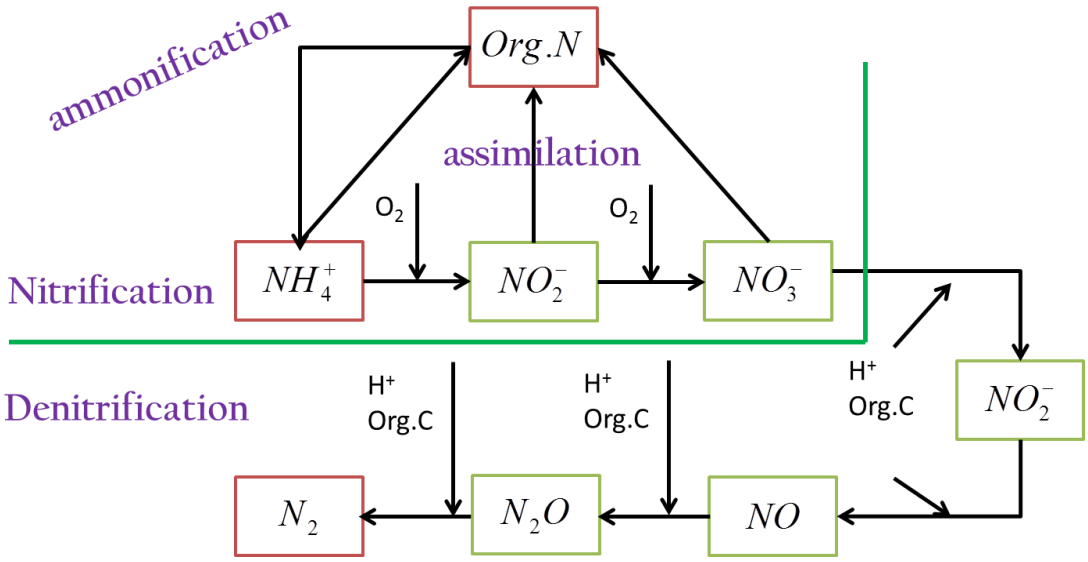


Figure 1-3 Nitrogen transformation in biological treatments.

NH_4^+ is a common reduced form of N and microbially transforms to NO_2^- and NO_3^- in the presence of oxygen. This process, called nitrification, is described below by Equation 1-1 and Equation 1-2 (Rittmann and McCarty 2000).

$$NH_4^+ + \frac{3}{2}O_2 \leftrightarrow NO_2^- + 2H^+ + H_2O$$ **Equation 1-1**

$$NO_2^- + \frac{1}{2}O_2 \leftrightarrow NO_3^-$$ **Equation 1-2**

Organic N can undergo ammonification and nitrification to NO_3^-. These microbial processes transform N but do not remove it from aquatic systems. N can be removed via assimilation, adsorption, and denitrification. Nitrogen assimilation is the process by which inorganic N (NH_4^+, NO_3^-, NO_2^-) is transformed into microbial or plant biomass and temporarily stored as organic N. NH_4^+ can also be removed through adsorption onto negatively charged soil particles. These two processes result in the temporary removal of N, whereas denitrification results in the permanent removal of N (Collins et al. 2010). Both anoxic conditions and a carbon source are necessary for biological denitrification. The process is described by Equation 1-3 using methanol (Rittmann and McCarty 2000).

$$6NO_3^- + 5CH_3OH \leftrightarrow 3N_2 + 5CO_2 + 7H_2O + 6OH^-$$ **Equation 1-3**

Moderate-to-poor ammonium and nitrate removal, with nitrate export observed in some instances, has been reported in bioretention system studies. The likely reason is that the nitrification process occurs in the bioretention cell between storm events (Davis et al. 2001; Hsieh and Davis 2005; Cho et al. 2009). Since nitrate is an anion, it cannot attach to soil and soil particles. It is very mobile and can easily be washed from the soil and transported into receiving waters (Davis and McCuen

2005). Promotion of denitrification is the element most critical to achieving effective nitrogen removal from stormwater runoff.

Some studies have reported that bioretention systems with an internal saturated zone can promote denitrification by creating anoxic conditions (Kim et al. 2003; Dietz and Clausen 2005b; Davis 2007; Hsieh et al. 2007b; Ergas et al. 2010). Ergas et al. (2010) conducted pilot-scale experiments with bioretention systems incorporating aerobic nitrification and anoxic denitrification zones with sulfur or wood chips as denitrification substrates. These experiments found more than 88% TN removal efficiencies in both units. Hunt's field-scale research performed in North Carolina showed a high capacity for nitrate removal (75%) with anoxic storage zones (Hunt et al. 2006). However, concentrations of TKN, NH_4^+ and TN in effluent were higher than in influent, a condition attributable to the conversion of organic forms of nitrogen to NH_4^+. Two bioretention cells were monitored at a study conducted on the University of Maryland campus; one cell contained an anoxic layer. Although no significant differences in the nitrate reductions by the two cells were reported, high mass removals of nitrate at 90% and 95% were observed. The results were attributed to a denitrification processes occurring in the saturated zones of both cells (Davis 2007).

Carbon sources, electron donors, contact time, composition of bioretention media, and vegetation are all important factors affecting the denitrification process. Kim et al. (2003) reported that using woodchips, alfalfa, and newspaper as carbon sources promoted 100% nitrate removal in a laboratory column study. Robertson

(2010) found that woodchips can work as long as 10 years as an effective carbon source for denitrification in agricultural runoff. In Smith's research, a longer contact time promoted denitrification (Smith 2008). Finer-textured soils support more denitrification due to their higher capacity for retaining water in soil microsites (Hunt et al. 2006; Hsieh et al. 2007b; Cho et al. 2009). Wood-based media, which are inexpensive, readily available, have considerable longevity and require a low level of maintenance are excellent electron donors for denitrification vaults (Robertson et al. 2005; Robertson 2010).

Pervious pavement is another recommended type of green infrastructure, which has been proven to be extremely effective in infiltrating stormwater runoff (Dietz 2007). Gilbert and Clausen (2006) conducted research in Connecticut which concluded that, as compared to asphalt driveways, the levels of nitrogen species (NO_3^-, NH_4^+, TKN) in the runoff from UNI Ecostone® driveways were significantly lower. A comparison of performance in controlling stormwater runoff was taken between porous pavements parking lot and asphalt parking lot by Dreelin et al. (2006). Porous pavements were found to have the advantage in treating metals and TP, but same effect was not found for TN.

Although numerous studies have been undertaken on the nitrogen-enhanced removal process for urban stormwater, single stormwater control measurements still lack the ability to effectively mitigate nitrogen concentrations. A combination of two or more technologies together is a promising possibility.

1.3 Research Objectives

The University of Maryland campus is located in the Anacostia River watershed, which is one of the most impaired rivers in the Chesapeake Bay watershed (Figure 1-4). As more people move to urban areas and more land is developed, high urban N and P pollution is becoming an increasingly critical problem. Currently, 300 million pounds of polluting nitrogen that reach the Chesapeake Bay each year (CBF 2014), which is causing major environmental challenges, but also opportunities, for stormwater retrofits, demonstrations, environmental justice, and education.

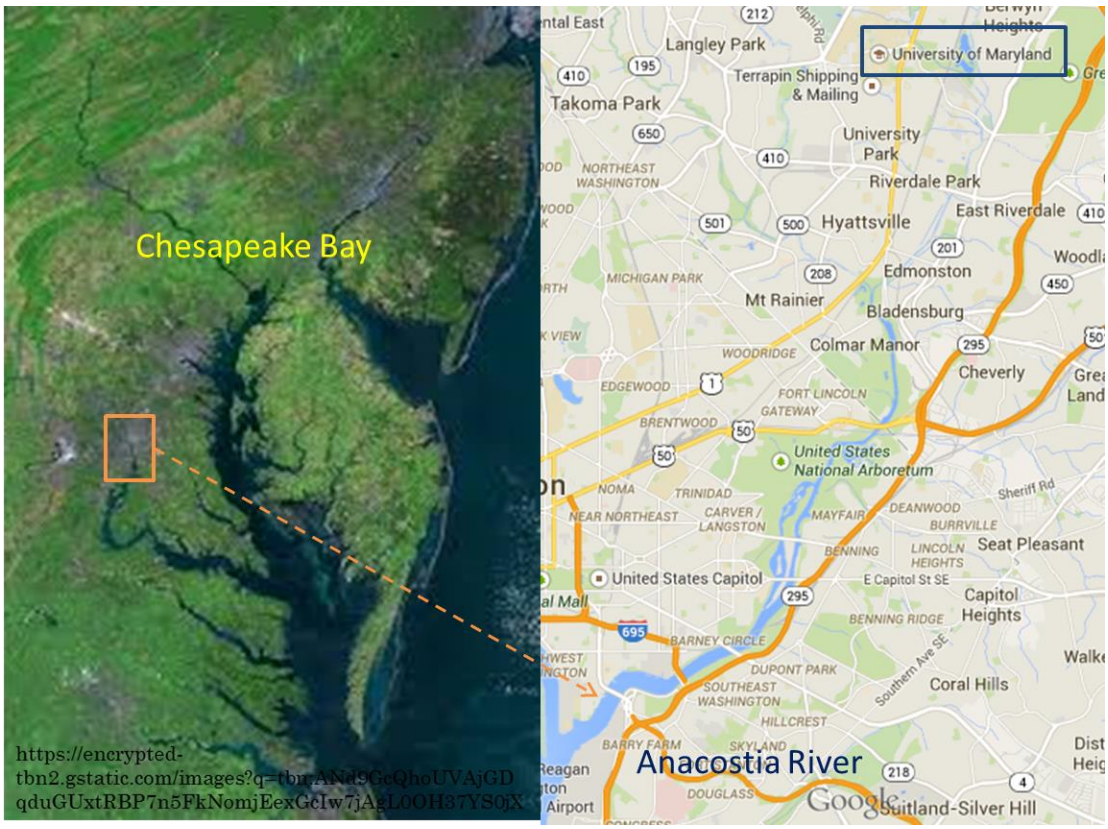


Figure 1-4 Chesapeake Bay watershed, Anacostia River and University of Maryland, College Park (http://maps.google.com/).

The overall goal of this project is to achieve significant nutrient load reductions from urban impervious surfaces without compromising hydraulic

conductivity. This was accomplished via two innovative SCMs on the University of Maryland campus located in College Park, Maryland. One project retrofitted an existing bioretention cell with an aluminum amendment to enhance phosphorus removal (P1 site). The other incorporated anoxic storage beneath a porous parking area to promote nitrogen removal (N1 site). The location of each cell is shown in Figure 1-5. These SMCs were constructed, rigorously monitored, and evaluated for nutrients load reductions. Specific objectives include:

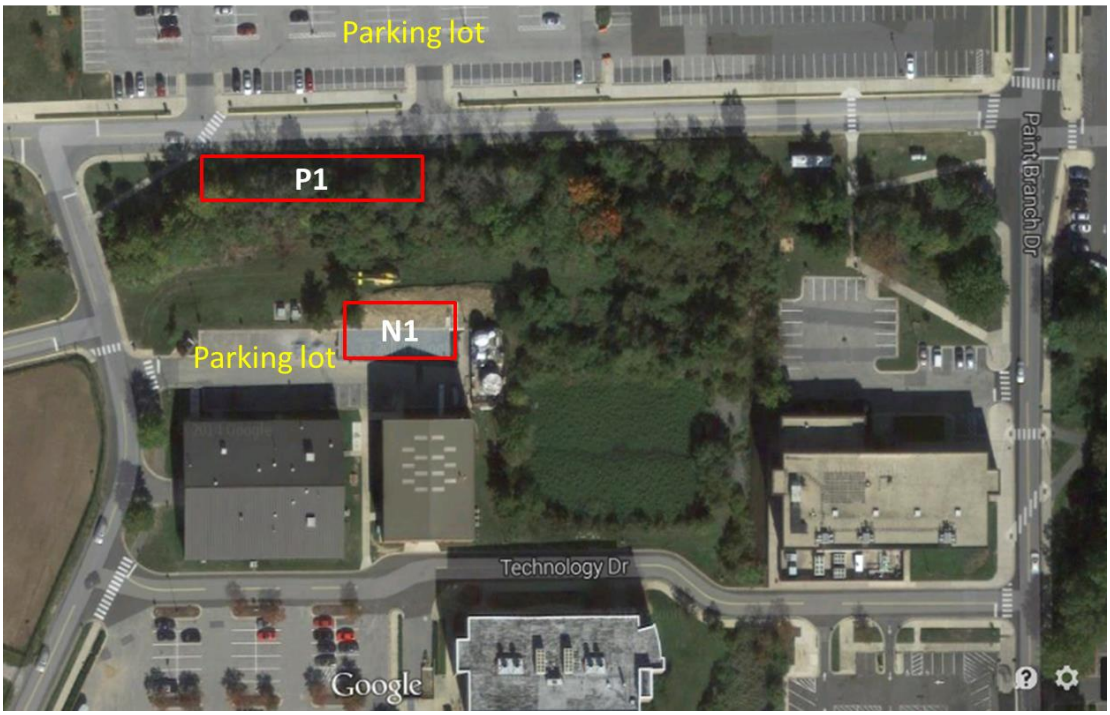


Figure 1-5 Locations of the monitored bioretention cells (http://maps.google.com/).

(i) Addressing the problem of SCMs that are ineffective with regards to nutrient (N, P) removal; (ii) Demonstrating how existing SCMs can be modified for the enhanced removal of nutrients from urban stormwater runoff, and providing the dissemination of design and performance information (ratio and depth of WTR applications with bioretention media; size and location of anoxic storage); (iii)

Clarifying the mechanisms of enhanced nutrient removal in bioretention systems (P removal mechanisms by Al-WTR application: anion bonding at mineral surfaces; N removal mechanisms under anoxic storage zones: denitrification.

The P1 project incorporated 5% (by mass) Al-WTR (recommended by O'Neill and Davis (2012b)) with an existing traditional bioretention cell (installed in 2004), which was rigorously monitored for two years, and TP concentrations higher in effluent than in influent were found (Li and Davis 2009). The construction was completed at the end of June, 2011 and the site was monitored from July 2011 to April 2013. Water quality data were monitored and pollutants mass loads were calculated to assess the discharge water quality and efficacy of the WTR retrofit cell (as compared to the site's previous performance), and to reveal the mechanisms of P species removal in field applications. Media samples were collected throughout the running period to evaluate the P distribution and movement in the media and to clarify the P transformation in the WTR amendment bioretention site.

The N1 project follows the research provided by a column study performed by Peterson (2013); the experiment combined porous pavement and denitrificaiton vaults in an attempt to achieve enhanced N removal. Water quality data were monitored and pollutant mass loads were calculated to evaluate the water quality of the porous pavement effluents and denitrification vault water, as well as the N species removal mechanisms; the experiment also evaluated the efficacy of the treatment train as compared to traditional bioretention systems in order to clarify the N transformation and removal by the new field system.

These technologies were rigorously monitored so that design and performance information could be disseminated as widely as possible to the engineering, academic, development, policy, campus, and regulatory communities, and so that these sites could be used as student and public education tools through both signs and displays.

Chapter 2: Bioretention Retrofit for Enhanced Phosphorus Removal: Hydrology and Water Quality

2.1 Introduction

Phosphorus (P) in urban stormwater results from fertilizers, automobile exhaust, living and decaying plants, animal remains and detergents (USEPA 1999). Although P is an essential nutrient for plant growth, excessive input to water bodies is a common cause of eutrophication and algal blooms in surface water, leading to poor water quality and loss of biodiversity (Stumm and Morgan 1996). As populations shift to urban areas and more land is developed, P is becoming a targeted pollutant in urban runoff.

Bioretention is a low impact development (LID) stormwater control measure (SCM) which has been proven as a technology to successfully manage flows and volume, and to mitigate a multitude of pollutants (Davis et al. 2001; Séby et al. 2001; Davis 2007; Bratieres et al. 2008; Li and Davis 2008a; Li and Davis 2009; Trowsdale and Simcock 2011). However, since P removal is complicated by possible leaching from the media and vegetation within various SCMs (Davis et al. 2009), the removal efficiency is highly variable, and the pollutant load reduction commonly results primarily from volume reduction (Li and Davis 2009).

Total phosphorus (TP) transported by stormwater runoff is comprised of particulate phosphorus (PP) and dissolved phosphorus (DP). Since traditional

bioretention relies on physical removal mechanisms such as sedimentation and filtration, bioretention is highly effective at removing PP, but is less successful at addressing DP. The effectiveness of the overall treatment is additionally complicated by the fact that P partitioning between particulate and dissolved phases is variable, depending on site specific conditions, with the particulate fraction ranging from 20% to > 90% of the total load (Cooke and Bruland 1987; Henderson 2008). DP removal in bioretention depends on chemical phosphorus sorption, complexation mechanisms to immobilize P species, and the geometry of the flow system (Davis et al. 2001).

Novel technologies, therefore, are necessary for enhanced P removal. WTRs are by-products from the coagulation process in drinking water treatment, which are high in aluminum (*Al* –) or iron (*Fe* –). Amendment of soil with WTRs was first suggested to mitigate P leaching from agriculture soils with limited P sorption capacity (Gallimore et al. 1999; Dayton et al. 2003; Novak and Watts 2005; Agyin-Birikorang et al. 2009). P adsorption occurs at WTR-hydrous iron/aluminum oxide interfaces; phosphate replaces hydroxyl (OH^-) groups or water molecules (H_2O) and then reorganizes into a very stable binuclear bridge through mono ligand and/or bidentate ligand exchange mechanisms.(Bohn et al. 1985)

WTR incorporation with traditional bioretention media has been demonstrated by both laboratory and pilot scale experiments to be an effective method for enhanced P removal (Lombi et al. 2010; Lucas and Greenway 2011). However, validated field data are limited. This chapter presents the hydrological and water quality performance of a WTR-enhanced bioretention site. In this field work, an existing traditional bioretention cell was retrofit with 5% (recommended by O'Neill and Davis (2012b))

WTR incorporation in order to enhance P removal. Total suspended solid (TSS) and phosphorus species TP, DP and soluble reactive phosphorus (SRP) were all monitored during rainfall events. The cell was first installed in 2004 and demonstrated excellent treatment performance for TSS and other water quality parameters, but less-effective performance for TP control (Li and Davis 2009). Ultimately, this work was undertaken to (i) assess discharge water quality and the efficacy of the WTR retrofit cell as compared to previous performance removing TSS and TP; and (ii) clarify the mechanisms of P species removal in field applications with WTR incorporation within a traditional bioretention system.

2.2 Methodology

2.2.1 Site Description

The enhanced-P site was created by retrofitting an existing bioretention cell (installed in 2004) on the campus of the University of Maryland, College Park, MD. It is trapezoidal in shape (length = 50.3 m, width = 2.4 m to 4.8 m; area = 181 m^2), with the media depth between 0.5 and 0.8 m; it manages stormwater runoff from a 2,800 m^2 asphalt parking lot, as well as roads and other concrete surfaces. The cell has a sloped surface with an average ponding storage depth of 15 cm. Two 15 cm perforated PVC pipes that run the length of this cell were installed below the media, collecting and conveying infiltrated water to the nearby Campus Creek (Li 2007b). A site picture and 3-D site configuration sketch are shown in Figure 2-1. P sources at this site are expected to be the same as in most parking lots, and include soil/dust deposition and vegetation detritus.

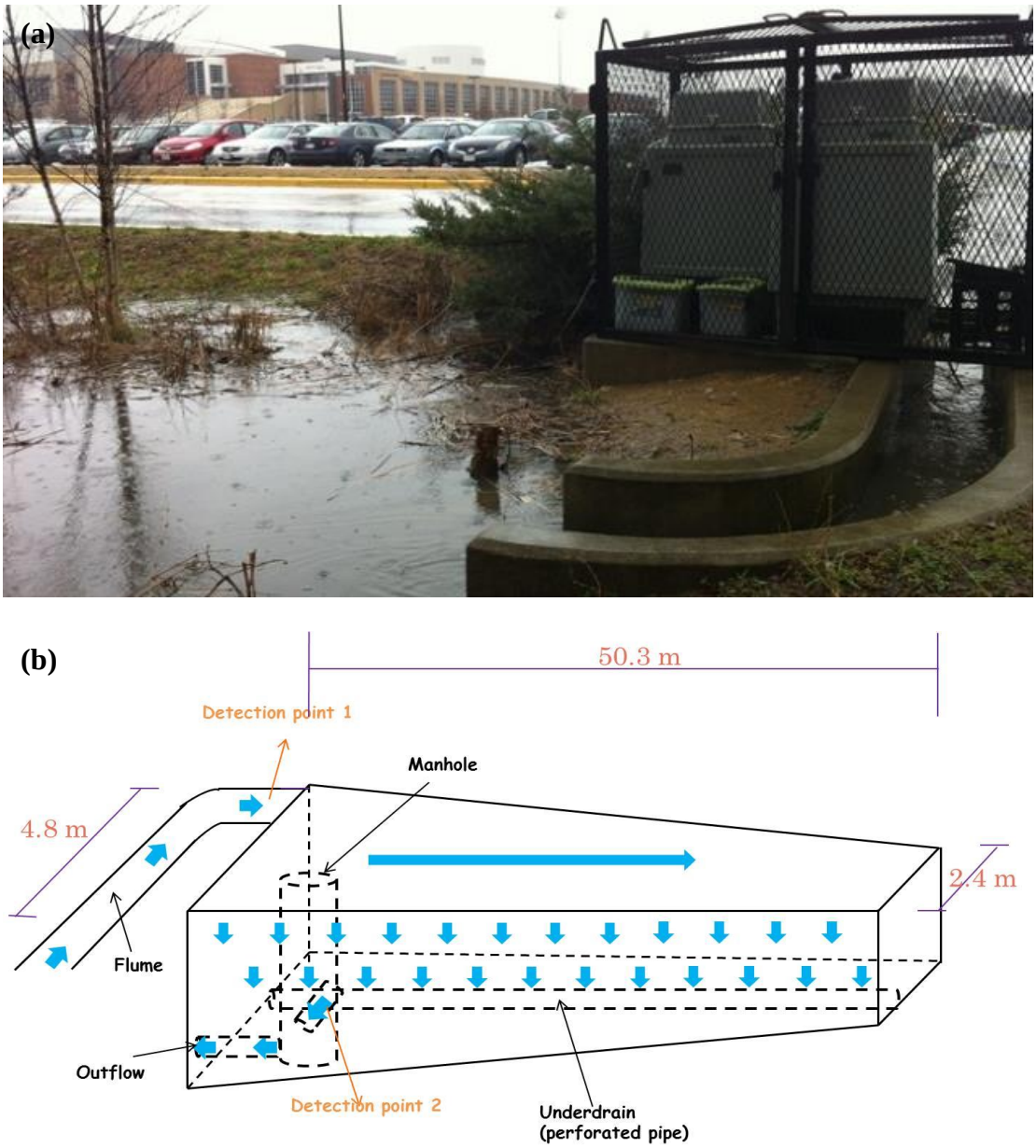


Figure 2-1 Enhanced P removal bioretention site diagram: (a) site picture; (b) 3-D site configuration sketch.

Approximately 5% WTR (air dry by mass) was employed to create the enhanced-P removal media. WTR obtained from the Rockville drinking water treatment plant in Potomac, MD, USA, were mixed with the top 40 cm of media at the site. Small vegetation at this site was cleared off and then replanted after the WTR

incorporation. The site retrofit process is shown in Figure 2-2. The site was studied for 22 months, beginning in July of 2011.

Figure 2-2 Enhanced P removal bioretention site retrofit process.

2.2.2 Monitoring and Sampling Methodology

The cell conveys incoming runoff through a 20 cm Cutthroat flume, and the underdrain was outfitted with a plug-in 20 cm Thel-Mar weir. ISCO 6712FR refrigerated autosamplers equipped with a bubble flow meter (730 Bubbler) were assigned to both the influent channel and underdrain effluent for flow measurement and water sampling. A recording rain gauge (674 Rain Gauge) with 0.0254 cm sensitivity was connected with one of the autosamplers to record rainfall depth. The stormwater runoff flow path and monitoring devices are shown in Figure 2-3.

Discrete sampling was employed for both inputs and outputs. The sampling program was set to collect twelve samples (350-mL glass sample bottles) per event, with different sample timing used to obtain more samples in the early part of the runoff event. Sample bottles were tap water and DI water cleaned first and then acid washed before placement in the sampler. All handling of sample bottles were done by gloved-personnel. Samples were picked up from the site within 24 hours and transported to the University of Maryland Environmental Engineering Laboratory for analysis. Samples for P analysis were acidified with H_2SO_4. All sample bottles were sealed, labeled, and then refrigerated (< 4°C) before testing. Parameters such as TSS and pH were tested immediately upon sample collection. Holding times for P species were < 7 days.

Figure 2-3 Stormwater runoff flow path and monitoring devices at enhanced P removal bioretention site

2.2.3 Analytical Procedures

The water quality parameters analyzed include pH, total suspended solids (TSS), TP, DP, and SRP (considered equal to dissolved phosphate); each analysis was performed using Standard Methods (APHA 2005). PP (PP = TP - DP) and dissolved organic phosphorus (DOP, DOP = DP - SRP) were calculated from direct P measurements. Sample pH was determined with a glass electrode pH meter (Mettler Toledo MA235, Greifensee, Switzerland). TSS was processed gravimetrically by Standard Method 2540 D. TP was analyzed using potassium persulfate digestion (4500-P B.5) and a colorimetric determination according to the ascorbic acid molybdenum blue method (4500-P E) at 880 nm (Shimadzu UV-160, Kyoto, Japan). DP and SRP samples were first filtered through a 0.22 μm membrane filter, then analyzed using methods identical to those employed in the TP analysis, except without the digestion process for SRP. A 5-cm pathlength cuvette was employed to provide a detection limit of 0.01 mg/L P.

2.2.4 Data handling and Statistical Analyses

Rainfall events were identified as discrete if they were separated by a dry period greater than 6 h. Runoff volumes, *V*, were calculated based on a simple numerical integration of flow measurements over time:

$$V = \sum Q(t)\Delta t \qquad \textbf{Equation 2-1}$$

Overall cumulative input/output pollutant masses, *M*, were calculated by:

$$M = \sum Q(t)C(t)\Delta t \qquad \textbf{Equation 2-2}$$

The Event Mean Concentration (EMC) is representative of the volume-weighted pollutant concentration throughout an entire event:

$$EMC = \frac{\int_0^{t_d} Q(t)C(t)dt}{\int_0^{t_d} Q(t)dt} \approx \frac{\sum C_i Q_i \Delta t_i}{\sum Q_i \Delta t_i}$$

Equation 2-3

where *C(t)* is the concentration; *Q* is the runoff flow rate; C_i is an individual concentration measurement; Q_i is the flow rate at the time concentration C_i was measured; and Δt_i is the time interval associated with C_i.

The annual pollutant mass loads produced or discharged per unit drainage area (L, kg/ha-yr) were calculated by:

$$L = \frac{MP}{AD}$$

Equation 2-4

where *M* is the overall cumulative input/output pollutant mass (kg) measured during this study; *P* is the average annual rainfall [107 cm/year for the State of Maryland; Maryland Department of the Environment (MDE) 2011]; *A* is the effective (runoff/rainfall) drainage area (ha) [0.6 × 0.28 ha for the site]; and *D* is the total rainfall depth (cm) measured during the study duration.

Exceedance probability plots were used to compare the rainfall distribution and cell performance. They were created by ranking the measured values from largest to smallest, and plotted on a log scale, implying their log-normal distribution nature, as described by Li and Davis (2009). Pollutant duration curves based on time-

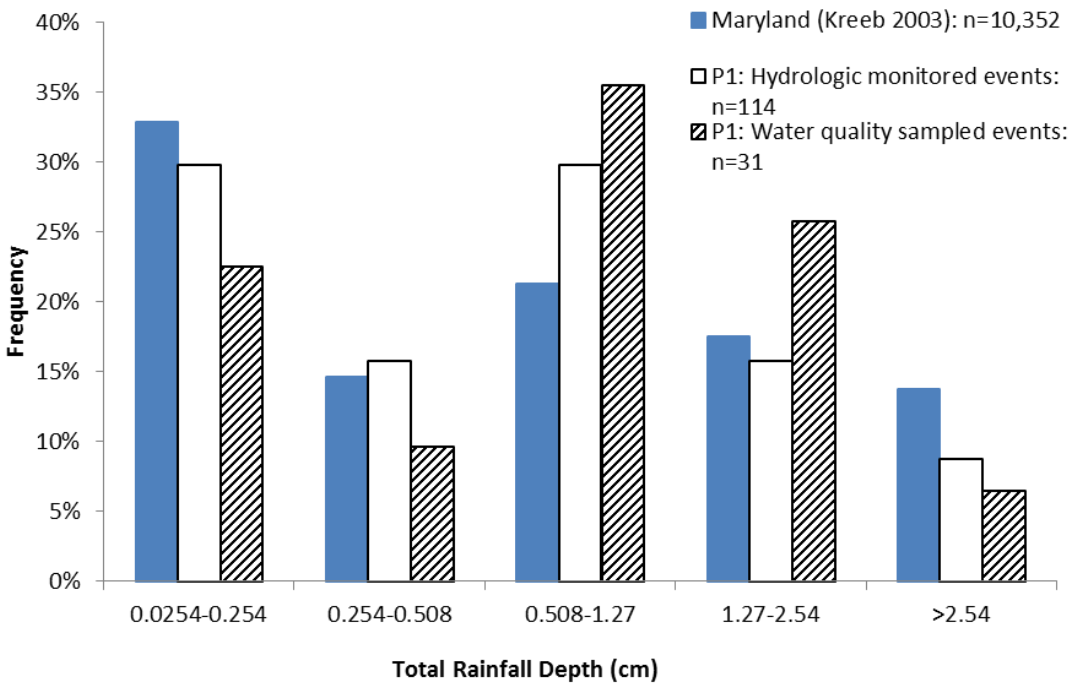
scheduled samples were created by plotting the individual sorted concentration values corresponding to the duration time in order to investigate concentration performance over time. A two-sample Student's t-test (Ayyub and McCuen 2002) and Wilcoxon sum-rank test were used to determine if the improvements in water quality and hydrologic performance were statistically significant.

2.3 Results and Discussion

From July 2011 through April 2013, 114 storm events were monitored, with 31 analyzed for water quality performance. These 114 storms represented all of the precipitation events occurring during the monitoring period, except for snow events and several events with faulty data due to equipment malfunction.

2.3.1 Hydrology

Storm Event Characterization. Events in this study were compared to Kreeb's (Kreeb 2003) study of historical rainfall duration and frequency for the State of Maryland in order to evaluate the representative nature of the monitored rainfall distribution at the P1 cell (Figure 2-4).



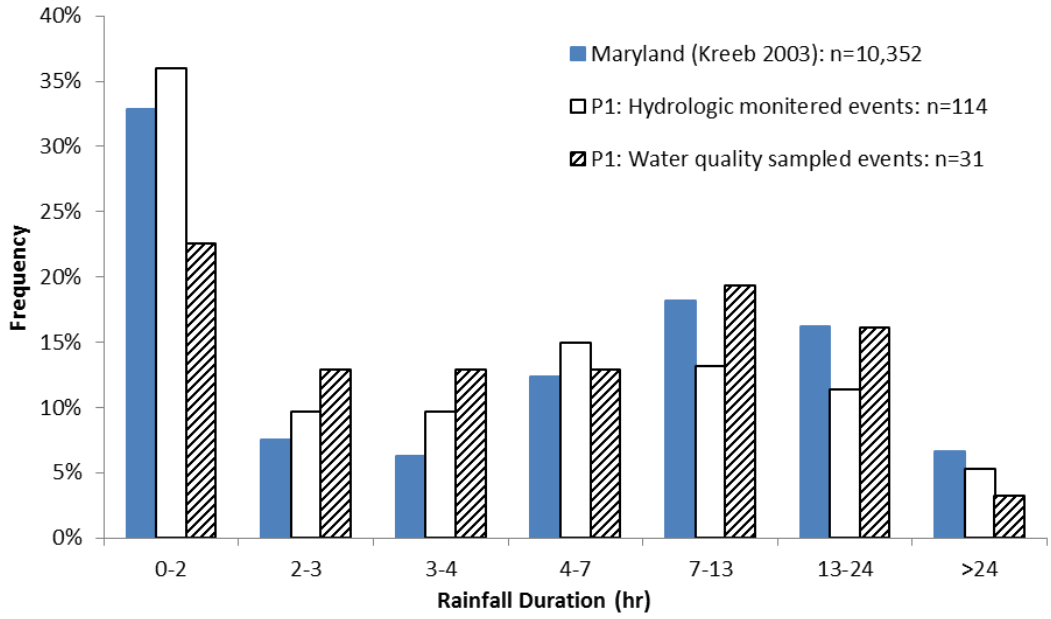


Figure 2-4 Rainfall depth and duration patterns for Maryland (Kreeb 2003) and enhanced P removal bioretention site storm events evaluated in this study.

The hydrologic monitored events exhibited a profile similar to typical Maryland storms in terms of rainfall depth, with a bias towards short to middle

rainfall durations (0 – 7 hr). The 31 events in which water quality was sampled had a greater occurrence of both middle and higher rainfall depths and durations. This likely resulted from a study focus on storms with both measurable influent and effluent for the water quality analysis, necessitating larger events. Overall, the sampling patterns reasonably reflected historical rainfall distributions during 2011-2013. The rainfall data are summarized as: during 114 monitored events, P1 received 0.025-12.52 cm rainfall (median = 0.699 cm), with an event duration of 0.03-65.5 hr (median = 3.4 hr), resulting in a rainfall intensity of 0.012-4.85 cm/hr (median = 0.166 cm/hr), and influent (inflow volume/drainage area) of 0.007-7.98 cm (median = 0.318 cm).

Volume Discharge Ratio. During the 114 monitored storms, 860 m^3 of stormwater was removed from the total 2,120 m^3 of runoff that entered the bioretention system, for a net reduction of 40%. The effluent/influent volume ratio (f_v) has been proposed as a way of using the capacity of bioretention storage to measure the success of low impact development (LID) performance (Davis 2008). It is calculated from:

$$f_v = \frac{V_{out}}{V_{in}}$$ **Equation 2-5**

where V represents the input and outlflow stormwater volumes. This parameter was determined and compared with the P1 values measured before WTR amendment at the site (Li et al. 2009) in order to determine the impact WTR

incorporation might have on volumetric performance in bioretention systems (Figure 2-5).

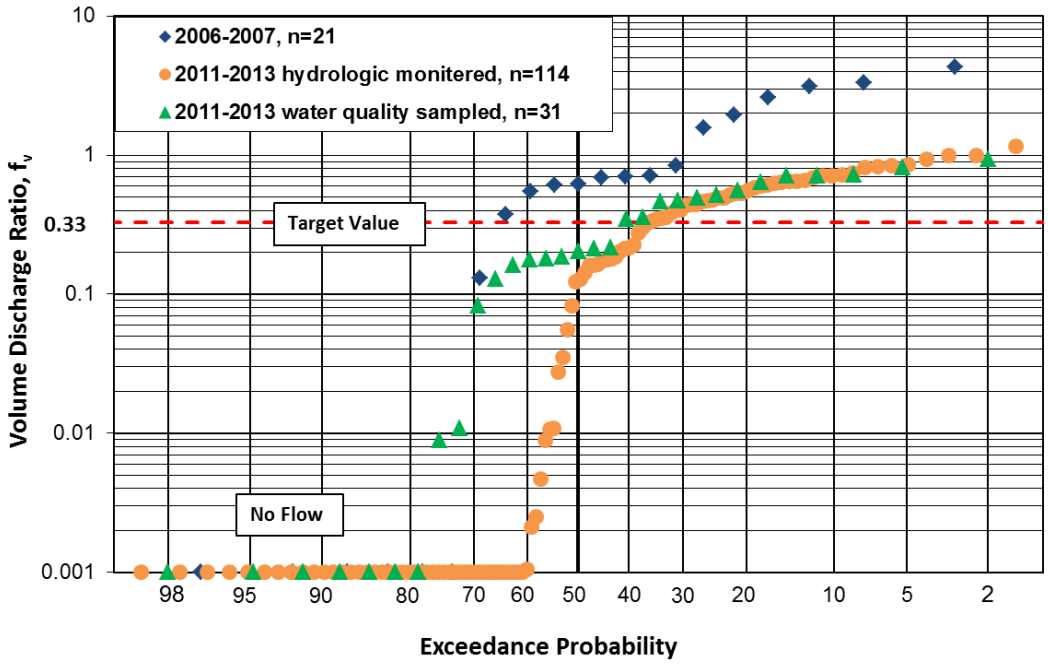


Figure 2-5 Volume discharge ratio exceedance probability plot for enhanced P removal bioretention site. Data in 2006-2007 were collected at the site before the enhanced P retrofit (Li 2007a; Li and Davis 2009).

The events in Figure 2-5 with $f_v > 1$ indicating output volumes greater than the input volumes are assumed to be caused by ground water surges from the nearby creek during intense or long-duration rainfall events (Li et al. 2009). Before the WTR retrofit, around 30% of the monitored events had $f_v > 1$; however, volume reduction was noted for more than 96% of all storm events occurring during the current study. The median f_v values are 0.622 (2006-2007 before retrofit), 0.205 (2011-2013 after retrofit, water quality sampled), and 0.144 (2011-2013 after retrofit, hydrologic monitored), indicating that the median input volume released decreased from more than 60% to only 20% after WTR application. Forty percent of all hydrologic events

monitored were small enough to be entirely captured by the bioretention facility, which is in agreement with the discussion in Li et al. (2009) where approximately 20% – 50% of the runoff entering the bioretention cells was lost to exfiltration and evapotranspiration.

The Wilcoxon rank-sum test compared the f_v values of the hydrologic monitored and water quality-sampled events that occurred after the retrofit. The null hypothesis ($\mu_1 = \mu_2$) could not be rejected even at the 10% significance level. This result shows that the f_v values for both data sets can be considered the same mean, suggesting that the events collected for water quality analysis were representative of typical hydrological performance during the monitoring period.

Comparing the hydrologic monitored events before and after the WTR amendment, lower f_v values after the WTR retrofit of the bioretention site were found to be statistically significant at the 99% confidence level. The low f_v values demonstrate the better efficacy of the bioretention media in managing water volume, although predictively quantifying the effect is somewhat complex. This better hydrologic performance may be attributable to (1) the high fraction of small storms during 2011-2013, as it has been noted in many investigations that hydrologic performance diminishes as rainfall depths increase and rainfall durations become longer (Li et al. 2009); and (2) somewhat larger cell media volume. A total of 1,500 kg of WTR were added to the bioretention site during retrofit, which resulted in an approximately 3 cm media depth increase. All in all, the WTR application to the bioretention media did not reduce the hydrologic capacity of the bioretention system.

Bioretention Abstraction Volume. The volumetric performance of output vis-a-vis input is presented in Figure 2-6, with a pattern similar to those reported by Davis et al. (2012). No discharge occurred for the small events and a linear relationship is noted between the input volume and discharge beyond a threshold; this indicates a fixed storage capacity (Bioretention Abstraction Volume, BAV) for the bioretention system, with some variation due to differences in rainfall intensities and antecedent conditions. For underdrained bioretention, the average BAV (Ave BAV) can be calculated by (Davis et al. 2012):

$$\text{Ave BAV} = \text{RZMS} \times (\text{SAT} - \text{WP}) + \text{LMS} \times (\text{SAT} - \text{FC}) \qquad \textbf{Equation 2-6}$$

where *RZMS* is the available media storage within the root zone; *LMS* is the lower media storage; and *SAT, WP,* and *FC* are the saturation, wilting point, and field capacity fraction, respectively.

After retrofit, the media was classified as loamy sand with a sand content of 82%, a clay content of 8%, and an organic matter content of 5.1%. The associated SAT (51.4%), FC (17.6%), and WP (9.5%) were found using the Soil-Water Characteristics model from Saxton and Rawls (2006). The RZMS (root zone = 10 cm) and LMS (lower media = 50 cm) in P1 site were 18.1 m^2 and 90.5 m^2, respectively. The field-determined BAV of 6.88 m^3 was much lower than the calculated Ave BAV (38.2 m^3), indicating that the bioretention cell was not fully utilized. This is attributable to the multidimensional flow mentioned by Davis et al. (2012), wherein underdrain flow is initiated in the area near the flow inlet; much less of the hydraulic load is transferred to the media further away from the outlet during larger events.

Changes in the characteristics of the bioretention cell after the WTR amendment could have contributed to this BAV loss. The cell had a sloped surface before amendment in order to encourage runoff coming into the cell to migrate as far as possible away from the inlet. However, the retrofit work may have modified the media slope.

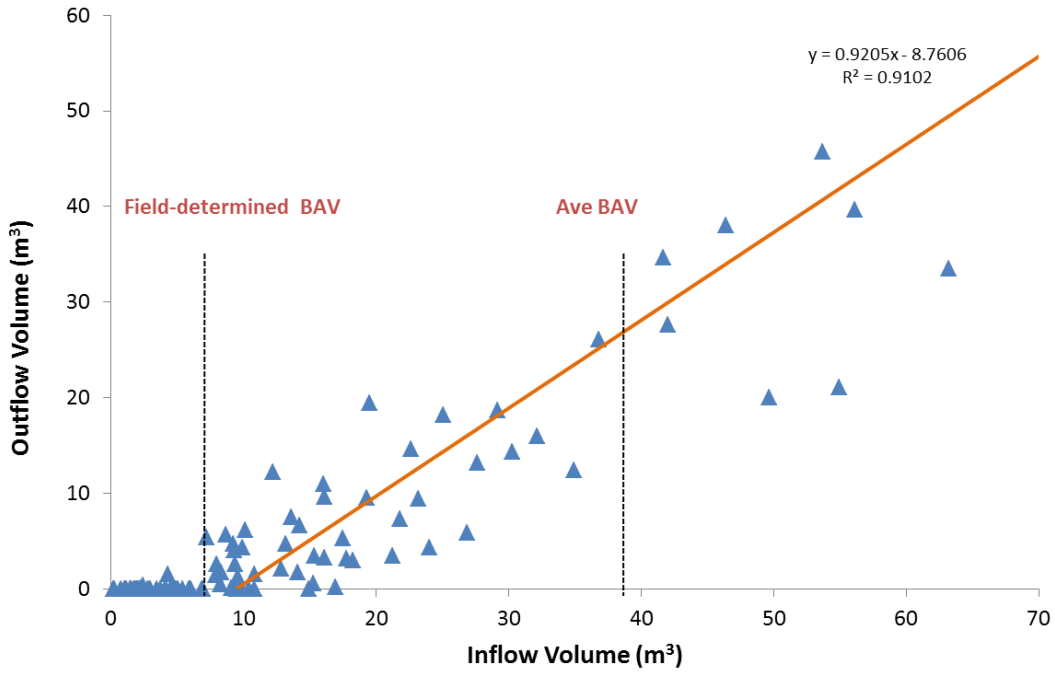


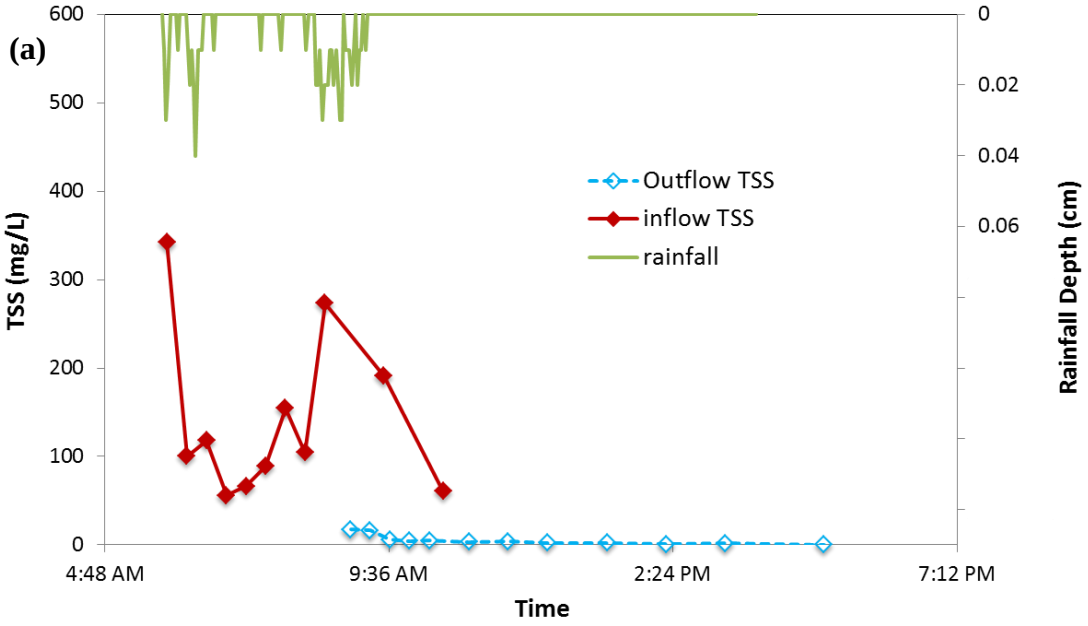
Figure 2-6 Volumetric performance for enhanced P removal bioretention site. Bioretention abstraction volume (BAV) calculated using Equation 2-6.

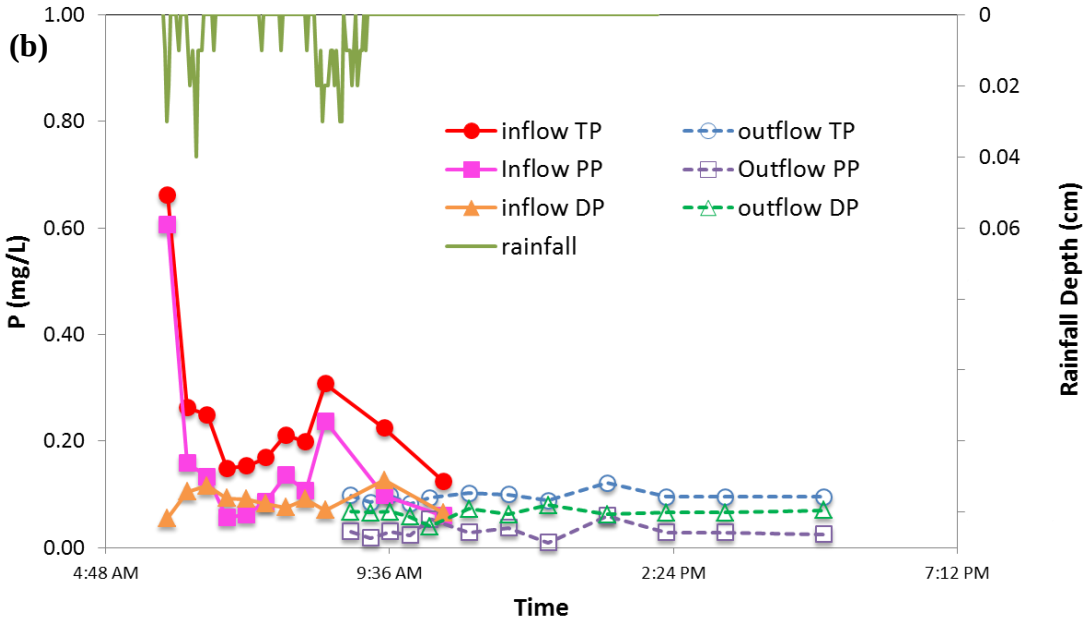
2.3.2 Water Quality

General Trend of a Storm Event. The sample input and output pollutant concentrations for TSS and P species on August 10, 2012 are presented in Figure 2-7 as an example of the general trends occurring during a storm event. The onset of the effluent sampling was delayed approximately three hours because it was a "multiple peaks" event. Since minimal underdrain discharge occurred from the first peak of

rainfall, the sampling program was triggered by the second peak (which was about two hours later than the first).

Significant reductions in TSS concentrations were noted during the event (Figure 2-7(a)). The influent TSS reached as high as 340 mg/L and the input EMC was 200 mg/L. The effluent TSS peak and EMC were 18 and 6.2 mg/L, respectively. The TP and PP concentration reductions were also obvious (Figure 2-7(b)); the peak decreased from 0.66 mg/L in influent to 0.12 mg/L in effluent for TP, and from 0.61 mg/L to 0.06 mg/L for PP. The effluent concentrations were not as variable as the influent concentrations due to the effective treatment and buffering of the incoming runoff by the bioretention system (Hatt et al. 2009). From Figure 2-7(c), it can be seen that the DOP was not significantly removed for this storm event. Both the influent and effluent EMCs were 0.03 mg /L. For SRP, the influent and effluent EMCs were 0.07 and 0.04 mg/L, respectively, indicating some removal. The influent SRP concentrations varied significantly, ranging from 0.02 to 0.11 mg/L. After the first several points, the output concentrations of SRP and DOP remained constant, at 0.04 mg/L and 0.03 mg/L, respectively. Data from the other events were generally similar, but differed in the details.


(a)
600
500
400
300
200
100
0
TSS (mg/L)
0
0.02
0.04
0.06
Rainfall Depth (cm)
Outflow TSS
inflow TSS
rainfall
4:48 AM
9:36 AM
2:24 PM
7:12 PM
Time


(b)
1.00
0.80
0.60
0.40
0.20
0.00
P (mg/L)
0
0.02
0.04
0.06
Rainfall Depth (cm)
inflow TP
outflow TP
Inflow PP
Outflow PP
inflow DP
outflow DP
rainfall
4:48 AM
9:36 AM
2:24 PM
7:12 PM
Time

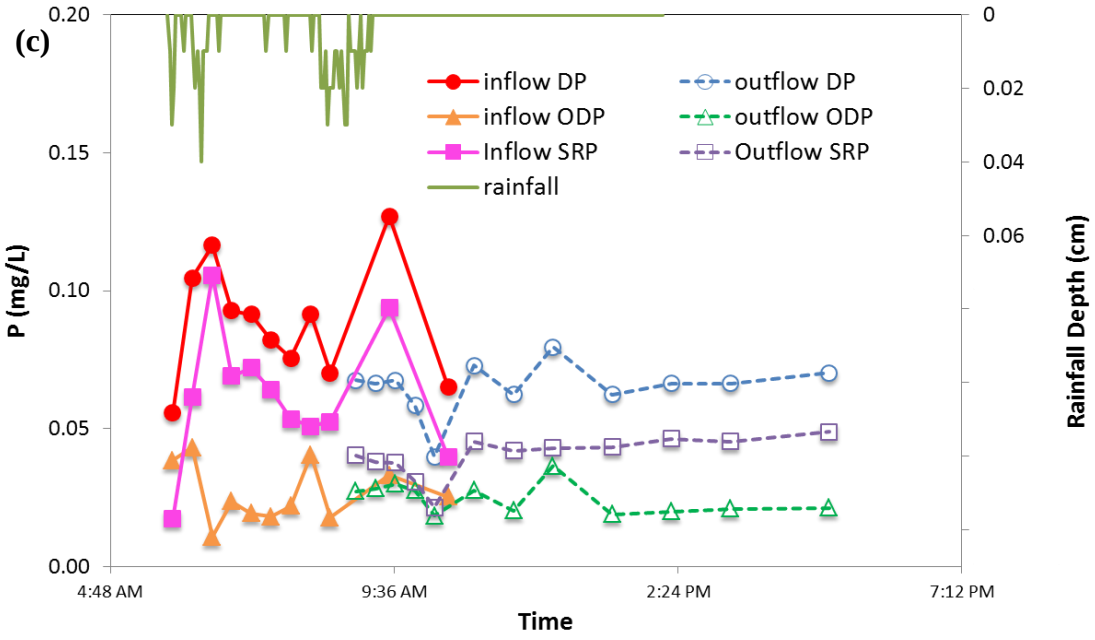
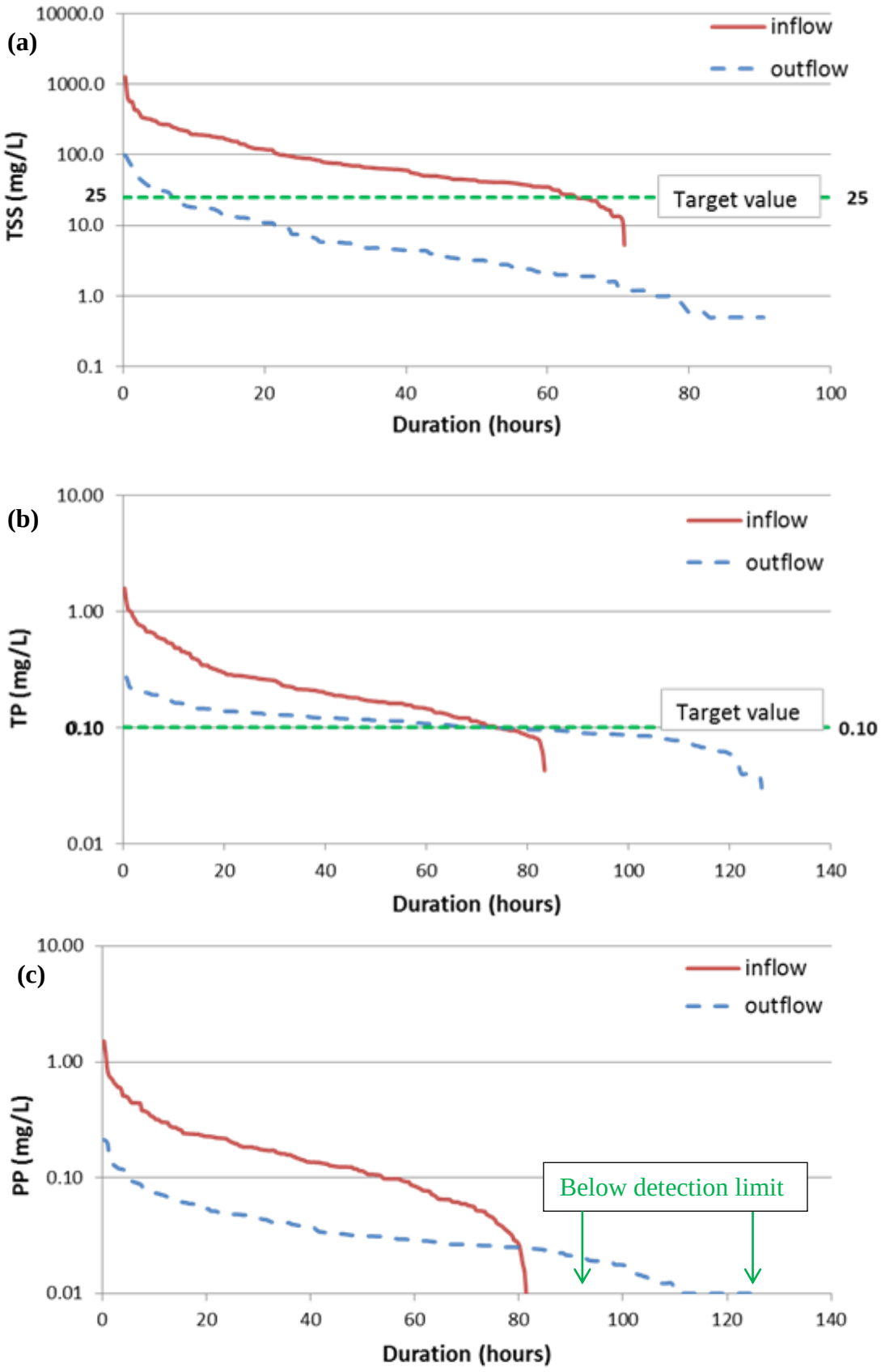


Figure 2-7 Water quality monitored at enhanced P removal bioretention site (August 10, 2012): (a) TSS concentrations; (b) P species (TP, PP, DP); and (c) P species (DP, SRP, ODP).

Table 2-1 EMCs for TSS and P species at enhanced P removal bioretention site.

	TSS in	TSS out	TP in	TP out	DP in	DP out	SRP in	SRP out	PP in	PP out	DOP in	DOP out
(a) All Sampled Events												
Total Events	26	15	30	18	30	18	21	12	30	18	21	12
EMCs (mg/L)												
Mean	127	7.8	0.33	0.11	0.11	0.07	0.07	0.04	0.22	0.04	0.06	0.03
Median	108	5.3	0.31	0.11	0.06	0.08	0.03	0.05	0.22	0.03	0.03	0.03
Max	298	33.4	0.81	0.17	0.66	0.11	0.28	0.07	0.37	0.08	0.61	0.05
Min	24	1.0	0.13	0.05	0.03	0.03	0.01	0.02	0.05	0.01	0.02	0.01
(b) Sampled Events with Outflow Collected												
Total Events	13		17		17		12		17		12	
EMCs (mg/L)												
Mean	142	8.8	0.29	0.11	0.07	0.07	0.05	0.04	0.21	0.04	0.03	0.03
Median	110	6.2	0.27	0.11	0.05	0.08	0.03	0.05	0.19	0.03	0.03	0.03
Max	298	33.4	0.61	0.17	0.26	0.11	0.22	0.07	0.37	0.08	0.06	0.05
Min	33	1.2	0.13	0.05	0.03	0.03	0.01	0.02	0.05	0.02	0.02	0.01
(c) Sampled Events without Outflow*												
Total Events	9		12		12		9		12		9	
EMCs (mg/L)												
Mean	127		0.41		0.17		0.08		0.23		0.11	
Median	118		0.35		0.13		0.05		0.24		0.06	
Max	223		0.81		0.66		0.28		0.31		0.61	
Min	78		0.27		0.03		0.01		0.14		0.02	

*Outflow had been entirely captured by enhanced P removal bioretention site or outflow volume < 0.5 m^3.


(a)
10000.0
1000.0
100.0
25
10.0
1.0
0.1
TSS (mg/L)
inflow
outflow
Target value
25
0
20
40
60
80
100
Duration (hours)
(b)
10.00
1.00
0.10
0.01
TP (mg/L)
inflow
outflow
Target value
0.10
0
20
40
60
80
100
120
140
Duration (hours)
(c)
10.00
1.00
0.10
0.01
PP (mg/L)
inflow
outflow
Below detection limit
0
20
40
60
80
100
120
140
Duration (hours)

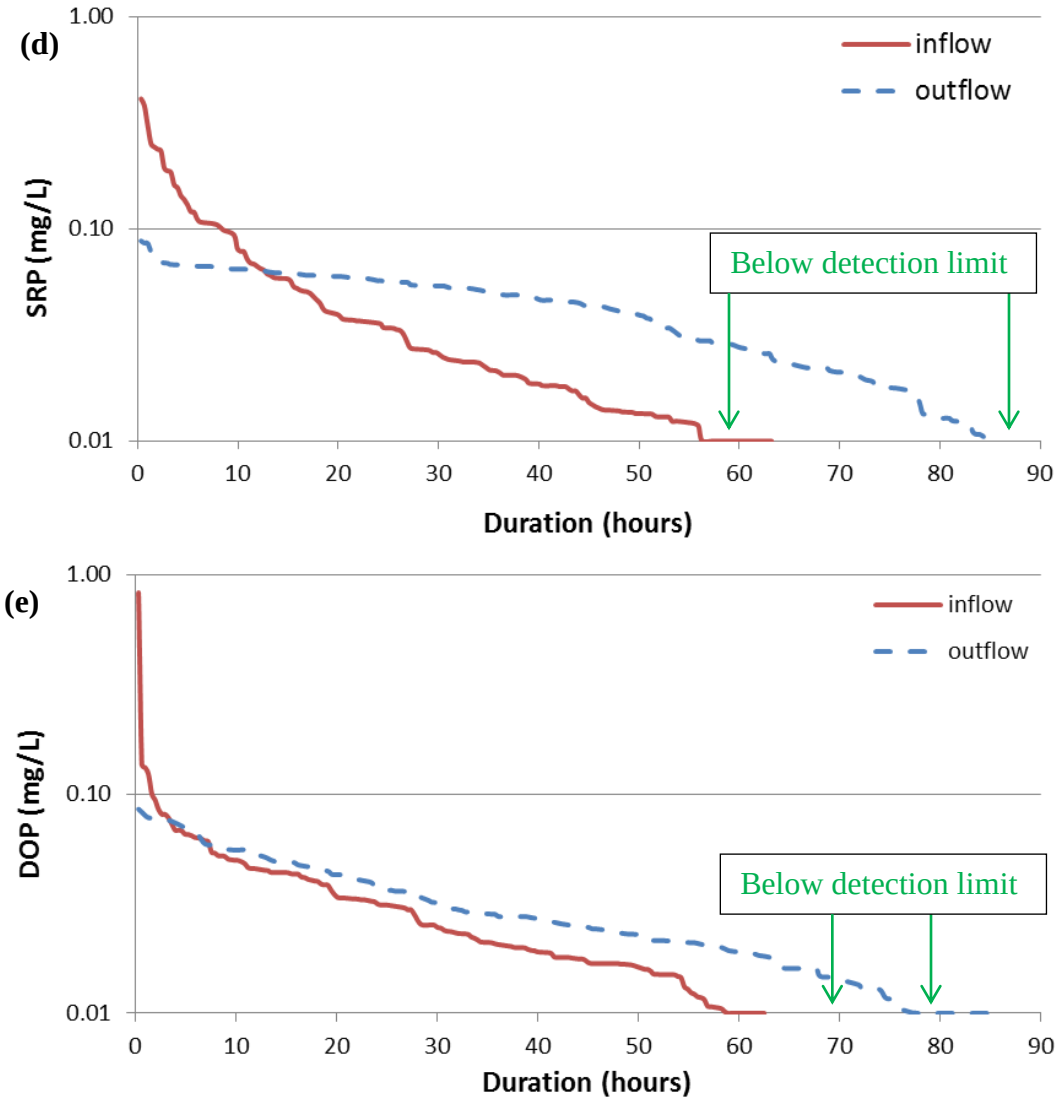


Figure 2-8 Pollutant duration curves for enhanced P removal bioretention site: (a) TSS; (b) TP; (c) PP; (d) SRP; and (e) DOP.

Water Quality Data Comparison and P Speciation. The detailed sampling results for TSS and P species are summarized in Table 2-1. The pollutant duration curves shown in Figure 2-8 were created to focus on the performance of discrete sample concentrations. Exceedance probability plots (Figure 2-9) were used to present water quality data in order to emphasize the treatment outcome and subsequent ecological impact of the discharge (Davis 2007). In addition to the results

from this study, comparisons of TSS and TP in both influent and effluent were made between the current data collected during 2011 – 2013 and the data collected in 2006 – 2007 (before the enhanced-P retrofit).

Total Suspended Solids. TSS demonstrated very good treatment performance and effluent quality for both the sample-based tests (for the pollutant duration curve, Figure 2-8(a)) and event-based tests (for the EMC exceedence probability plot, Figure 2-9(a)), which agree with previous studies on this site (Li and Davis 2009). From Figure 2-8(a), it can be seen that input discrete runoff TSS concentrations ranged from 5 to 1274 mg/L (median = 76 mg/L), whereas discharge TSS ranged from less than 1 to 99 mg/L (median = 5 mg/L). The bioretention discharge met the 25 mg/L TSS target level criterion (Davis and McCuen 2005) 92% (83.6 hr out of 90.5 hr) of the discharge time, compared to only 9% (6.61 hr out of 70.84 hr) for the influent.

TSS removal is dominated by the settling and filtration prompted by the bioretention media (Li and Davis 2008b; Li and Davis 2008c). Steady state particulate matter removal (C/Co) is predicted by the fundamental filtration model (Yao et al. 1971; Cleasby and Logsdon 1999):

$$\frac{C}{C_0} = \exp\left(-\frac{3}{2}\frac{(1-\varepsilon)}{d_c}\alpha\eta_o L \right) \qquad \textbf{Equation 2-7}$$

where ε is the filter porosity; α is the sticking coefficient; d_c is the collector diameter; and d_p is the particle diameter. The parameter η_o is the overall collector efficiency, which is the sum of three individual collector efficiencies: sedimentation

($\eta_s = \frac{(\rho_s - \rho)gd_p^2}{18\mu V}$), interception ($\eta_I = \frac{3}{2}\left(\frac{d_p}{d_c}\right)^2$) and diffusion

($\eta_D = 0.9\left(\frac{kT}{\mu d_p d_c V}\right)^{2/3}$). By employing realistic bioretention values for the parameters of Equation 2-7 (ε = 0.4, α = 0.1, d_c = 0.2, d_p = 0.05) (Davis and McCuen 2005), a predicted removal of 96% was found, supporting the conclusions of an effective filtration mechanism in bioretention. The intermittent, variable, heterogeneous non-steady state urban particle loadings occurring in stormwater runoff can account for the slightly higher than predicted effluent TSS concentrations (Li and Davis 2008b).

Figure 2-9(a) presents TSS EMCs of the influent compared to the corresponding effluent for events with both inflow and outflow during 2006-2007 (before WTR retrofit) and 2011-2012 (after retrofit). The inflow TSS EMCs ranged from 7 to 422 mg/L before, and from 24 to 298 mg/L during the current study. The outflow TSS concentrations were low during both monitoring periods. All except one of the events met the 25 mg/L target level criterion after WTR incorporation.

The Wilcoxon rank-sum test evaluation found that the TSS concentrations were significantly (α = 1 %) reduced by the bioretention cell for both the current and previous data periods. Both the inflow and outflow concentrations showed no dissimilar behavior between the two monitoring periods at α = 1%. The results demonstrate that WTR incorporation did not harm the bioretention media's filtration performance.

Total Phosphorus. The cumulative pollutant duration curve for TP is shown in Figure 2-8(b). The concentrations for the inflow ranged from 0.04 to 1.58 mg/L (median = 0.21 mg/L), whereas the outflow ranged from 0.03 to 0.27 mg/L (median = 0.11 mg/L), indicating effective treatment. Forty-two percent (53.4 hr out of 126.3 hr) of the discharge time for the effluent met the 0.1 mg/L target level criterion (USEPA 1986) compared to only 12% (9.61 hr out of 83.4 hr) for the influent.

The TP EMC data for the two monitoring periods are compared in Figure 2-9(b). Influent EMC values for TP during the previous and current studies ranged from 0.05 to 0.74 mg/L (median = 0.14 mg/L) and 0.13 to 0.81 mg/L (median = 0.31 mg/L), respectively. Corresponding effluent concentrations ranged from less than 0.05 to 0.51 mg/L (median = 0.32 mg/L) before retrofit and 0.05 to 0.17 mg/L (median = 0.11 mg/L) after retrofit (A 1-cm pathlength cuvette was employed in the previous research and the detection limit was 0.05 mg/L P). A comparison of the data sets using a Wilcoxon rank-sum test indicated that (i) TP leaching occurred before WTR incorporation (output > input); (ii) although the TP input was higher (α = 1%) compared to the 2006 – 2007 period, TP concentrations were significantly reduced (α = 1%) after treatment through the WTR bioretention media; and (iii) the effluent TP concentrations were much lower (α = 1%) than they were before the WTR retrofit.

The bioretention cell was not effective for TP removal during the previous study, where it was concluded that the media had a high phosphorus content, causing TP export (Li and Davis 2009). TP export from traditional bioretention media has also been noted by others (Dietz and Clausen 2005a; Hunt et al. 2006). However, in this research after WTR incorporation the media was shown to be effective for

treating TP, which is attributable to the increase of P adsorption capacity contributed by the WTR (Dayton and Basta 2005a; Novak and Watts 2005; O'Neill and Davis 2012a; O'Neill and Davis 2012b).

Phosphorus Speciation. The sample-based pollutant duration curves for PP are presented in Figure 2-8(c), indicating excellent removal. PP concentrations in the inflow varied significantly, ranging from 0.01 to 1.51 mg/L; the median value was 0.15 mg/L. However, PP decreased significantly after the runoff passed though the bioretention media; the values were lowered to less than 0.01 to only 0.21 mg/L (median = 0.03 mg/L). For more than 96% (119.1 hr / 124.7 hr) of the time, the effluent concentrations were lower than 0.1 mg/L, whereas the influent met this criterion only 34% (27.5 hr / 81.4 hr) of the time. The exceedance probability plot for PP (Figure 2-9(c)) also showed very good treatment performance. The median EMC of the inflow and outflow for all of the collected events was 0.22 mg/L and 0.03 mg/L, respectively, values which were close to the sample-based results.

The mean and median event-based dissolved fractions ($f_d = \frac{DP}{TP}$) were 0.31 and 0.28, illustrating that PP was the dominant species in the surface runoff, in accordance with research by Berretta and Sansalone (2011). After passage through the bioretention media, the mean and median f_d in the discharge increased to 0.67 and 0.68, indicating that the PP removal was better than DP removal.

The Wilcoxon rank-sum test indicated that the PP concentrations were significantly reduced (α = 1%) by the enhanced bioretention system. PP is managed with TSS, which causes it to settle and become filtered from the influent (Davis 2007).

Although no PP or DP data were collected in the prior study (2006 - 2007), it can be assumed that the PP removal performance should have been good before the retrofit because the TSS removal was very good. As a result, the leaching of TP that was noted at this site (Li and Davis 2009) may be attributable to the leaching of DP, likely from organic matter in the media.

SRP and DOP. The Wilcoxon rank-sum test indicated a net removal of neither SRP nor DOP from incoming runoff (Figure 2-9(d) and Figure 2-9(e)). The influent EMCs for SRP and DOP ranged from approximately 0.01 to 0.28 mg/L and 0.02 to 0.61 mg/L, respectively, and the effluent EMCs were consistently between 0.02 to 0.07 mg/L and 0.01 to 0.05 mg/L. The pollutant-duration curves (Figure 2-8(d), Figure 2-8(e)) show that the inflow concentrations for both SRP (less than 0.01 mg/L to 0.41 mg/L, median = 0.03 mg/L) and DOP (less than 0.01 to 0.83 mg/L, median = 0.03 mg/L) varied over more than an order of magnitude, yet the outflow concentrations were relatively stable. Concentrations ranged from less than 0.01 to 0.09 mg/L for both, and the median value was less than 0.03 mg/L for DOP and 0.04 mg/L for SRP. These data agree with the trend presented in Figure 2-7(c) for a single event. After the first several points (about 2 hrs), the output concentrations of SRP and DOP remained essentially constant.

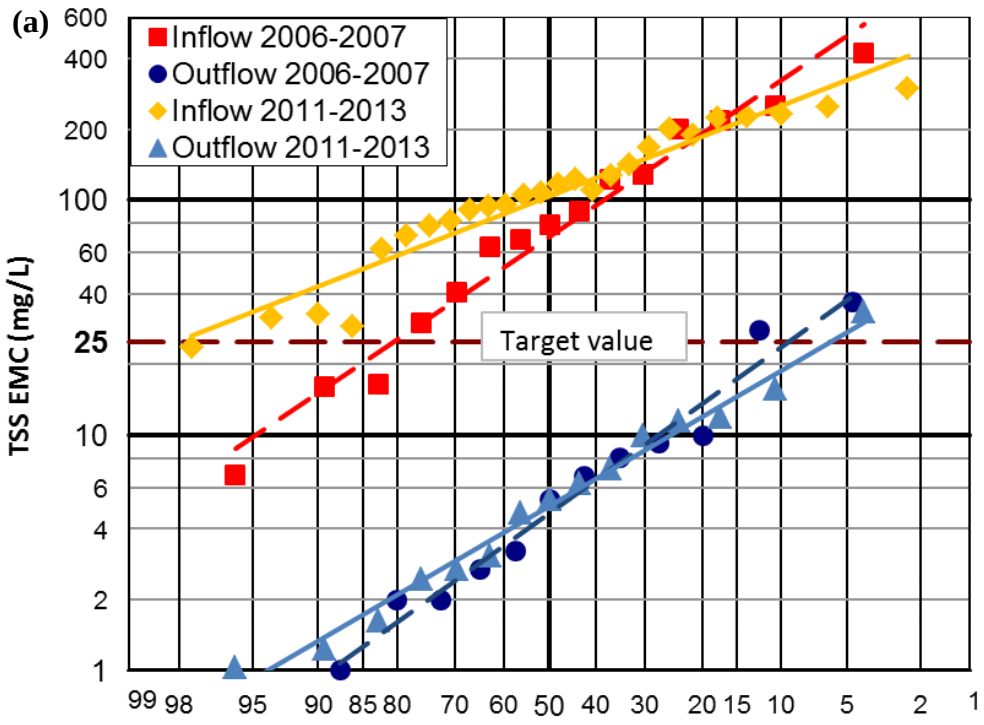
Previous research has shown that in long-term scenarios, PP filtered and accumulated from urban stormwater may potentially partition back to the aqueous phase (Scarlatos 1997; Chen and Sheng 2005; Berretta and Sansalone 2012), and biological processing may cause DOP to export (Lucas and Greenway 2011). Although this study of an enhanced-P treatment system examines and finds no DP

loss from input, no leaching of DP was noted, indicating that any release of DP from the media's organic constituents and vegetation litter was not leached from the system.

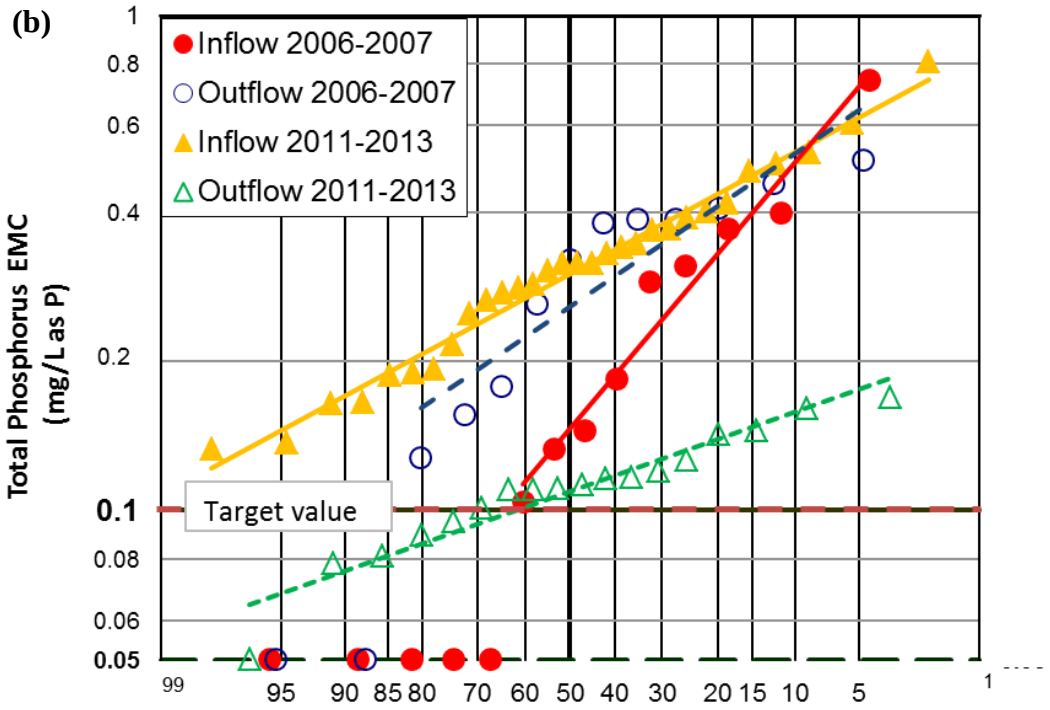
The major mechanisms of P retention in the bioretention media include adsorption and/or precipitation, since microbial and plant uptakes account for only a small fraction of the P retained (Lucas and Greenway 2008; Lucas and Greenway 2011). Phosphorus retention mechanisms can be considered a combination of a fast reversible true sorption process on soil particle surfaces, plus various slower time-dependent processes that have been described as "slow adsorption", "slow reaction", "deposition", "fixation", precipitation" or "solid-state diffusion" (Stumm and Morgan 1996; McGechan 2002; Wu and Sansalone 2013). After being retained, inorganic phosphorus species, which typically are considered bioavailable, can be utilized by vegetation growth in the bioretention facility (Davis et al. 2006). Hsieh et al. (2007a) found that long-term phosphorus reactions regenerate active short-term sorption sites in repetitive bioretention columns. In this research, most of the retained phosphorus in the media layers was available for vegetative uptake, and environmental risk thresholds were not exceeded.

The nearly constant output of SRP and DOP suggest an adsorption mechanism in which a constant equilibrium concentration is discharged from the media. Given adequate time, P will find reactive sites in micropores, becoming more strongly adsorbed at the individual surface sites (Ippolito et al. 2003). Erickson et al. found similar results in the investigation of phosphate removal from synthetic stormwater by a sand filter amended with iron filings (Erickson et al. 2007; Erickson et al. 2012). An adsorption equilibrium mechanism explains the steady state dissolved P

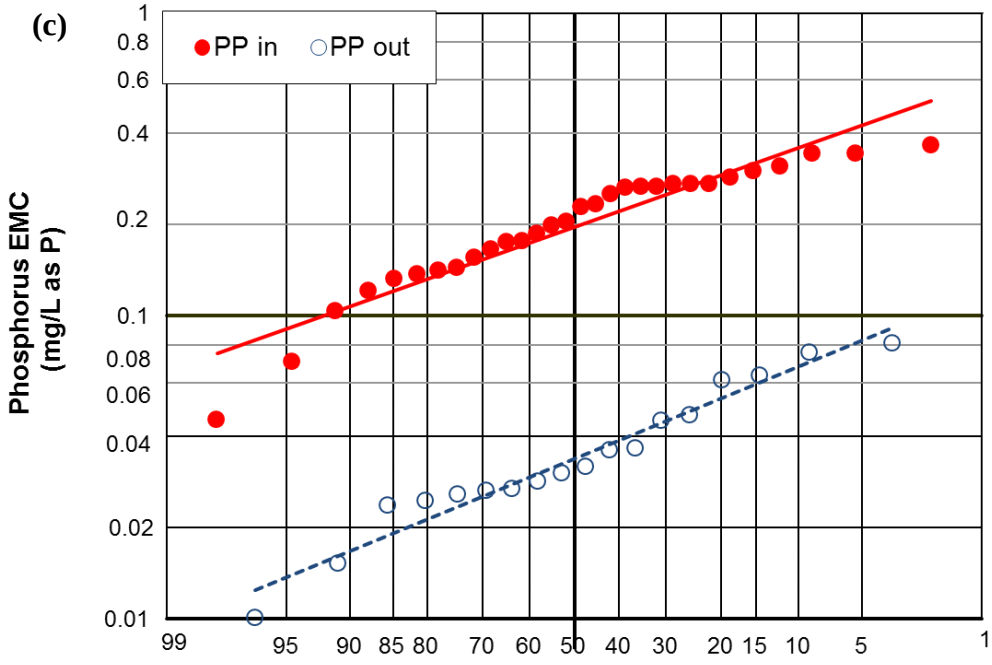
concentrations observed in our study, as well as others, including those that are higher than the influent concentrations. The SRP and DOP existed at nearly equal fractions of DP in the incoming runoff, whereas SRP accounted for 59% of the DP in the effluent. Moreover, as mentioned above, DOP can leach from captured PP and microbial processes occurring in the media (Scarlatos 1997; Chen and Sheng 2005; Berretta and Sansalone 2012). This suggests that WTRs have the ability to sorb DOP. A schematic of various sources and fates of P species in bioretention systems is presented in Figure 2-10.



(b)


Inflow 2006-2007
Outflow 2006-2007
Inflow 2011-2013
Outflow 2011-2013
Target value
Total Phosphorus EMC (mg/L as P)
1
0.8
0.6
0.4
0.2
0.1
0.08
0.06
0.05
99
95
90
85
80
70
60
50
40
30
20
15
10
5
1

(c)


PP in
PP out
Phosphorus EMC (mg/L as P)
1
0.8
0.6
0.4
0.2
0.1
0.08
0.06
0.04
0.02
0.01
99
95
90
85
80
70
60
50
40
30
20
15
10
5
1

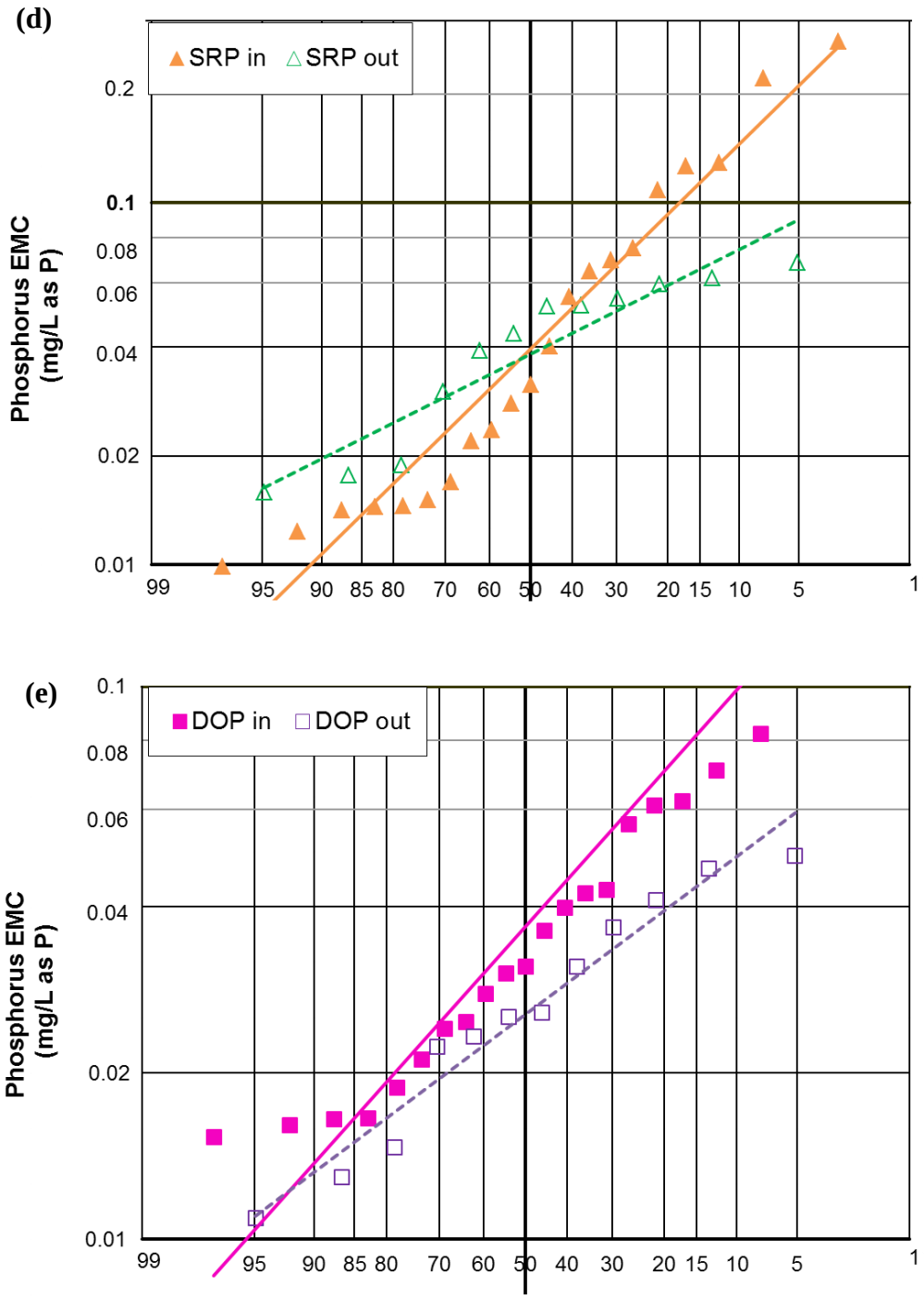


Figure 2-9 Exceedance probability plots for enhanced P removal bioretention site: (a) TSS; (b) TP; (c) PP; (d) SRP; and (e) DOP. (Data in 2006-2007 were collected at the same site before the enhanced P retrofit (Li 2007a; Li and Davis 2009)).

Pollutant Mass Load Reduction. Annual pollutant loads were calculated for individual storm events using Equation 2-4. The pollutant mass reduction (or increase) ratio, R_m, was calculated by:

$$R_m = 1 - \frac{L_{out}}{L_{in}} \qquad \textbf{Equation 2-8}$$

Pollutant load reduction for stormwater runoff passing through the bioretention system consisted of reductions both in volume and pollutant concentration. This reduction can be envisioned as: (i) when water enters the cell, treatment/adsorption takes place at the media surface (Li and Davis 2008a; Li and Davis 2008b) designated as the system treatment; and (ii) the stormwater volume is reduced by percolation, storage, and/or evapotranspiration. Mass reductions in the latter case are based on volume reduction.

The pollutant mass load reduction due to volume reduction, $L_{v\text{-}red}$, was estimated by summing the product of the runoff volume reduction and discharge concentration for each storm. If zero discharge occurred, the mass reduction was attributed entirely to volume reduction. The cumulative input and output pollutant EMCs and loads for the cell during 2006-2007 and 2011-2013 and the mass volume reduction ratio, R_{mv}, accounted for the fraction of $L_{v\text{-}red}$ responsible for the total mass reduction are listed in Table 2-2; the P species comparisons of overall pollutant mass loads between influent and effluent are shown in Figure 2-10.

Table 2-2 Comparison of the influent and effluent water quality and pollutant mass loads for water quality sampling events at the enhance P removal bioretention site in 2006-2007 and 2011-2013. (Data in 2006-2007 were collected at the same site before the retrofit (Li 2007a; Li and Davis 2009)).

Pollutant	Input EMC (mg/L)[a]	Output EMC (mg/L)[a]	L_{in} (kg/ha-year)	L_{out} (kg/ha-year)	R_m	L_{vred} (kg/ha-year)	R_{mv}
2006-2007							
TSS[c]	137	8	890[b]	32[b]	96.4%		
TP[c]	0.41	0.27	2.7[b]	1.2[b]	55.1%		
2011-2013							
TSS[d]	97	6	1090	47	95.7%	106	10.2%
TP[e]	0.300	0.111	3.0	0.48	84.0%	0.79	31.4%
DP[e]	0.070	0.065	0.70	0.28	59.9%	0.40	95.6%
PP[e]	0.230	0.046	2.3	0.20	91.3%	0.39	18.6%
SRP[e]	0.041	0.037	0.41	0.16	60.3%	0.22	91.1%
DOP[e]	0.030	0.028	0.30	0.12	59.3%	0.18	~100%

[a]Based on the cumulative mass divided by the cumulative volume for all collected samples.
[b]Calculated using Equation 2-4.
[c]12 events.
[d]20 events.
[e]17 events.

Both EMCs and mass loads were reduced for TSS and all P species. Moreover, pollutant mass removals were higher than EMC removals due to the attenuation of volume by the bioretention media. TSS had a pollutant mass removal of 95.7%, which was close to the value recorded before the WTR amendment (96.4%), again indicating that the bioretention filtration mechanism was not affected, but also that volume management was not compromised. The TP mass removal was improved by the retrofit. Before retrofit, the load was reduced from 2.7 to 1.2 kg/ha-yr; the new reduction, from 3.0 to 0.48 kg/ha-yr, supports the assertion that WTR incorporation enhanced the P sorption capacity of the media, resulting in an effective TP treatment (Table 2-2).

The inflow PP mass proportion of TP was 76.6%, and reduced to about 41.5% in the outflow. The total runoff P reduction was dominated by PP (83.3%). The SRP fractions of DP were similar in both inflow (57.8%) and outflow (57.2%), a bit higher than DOP. The enhanced bioretention system reduced the SRP mass by 60.3% and DOP by 59.3% (Table 2-2), which suggests that they were removed by similar (sorption) mechanisms. Although Table 2-2 indicates that the DP mass reduction resulted almost entirely from the volume reduction (95.6%), this analysis does not consider any leaching of DP from the media or captured PP; both are expected to contribute to the P that is treated and accumulated by the media (Figure 2-10). Overall, amendment with Al-WTR decreased DP mass by approximately 60%.

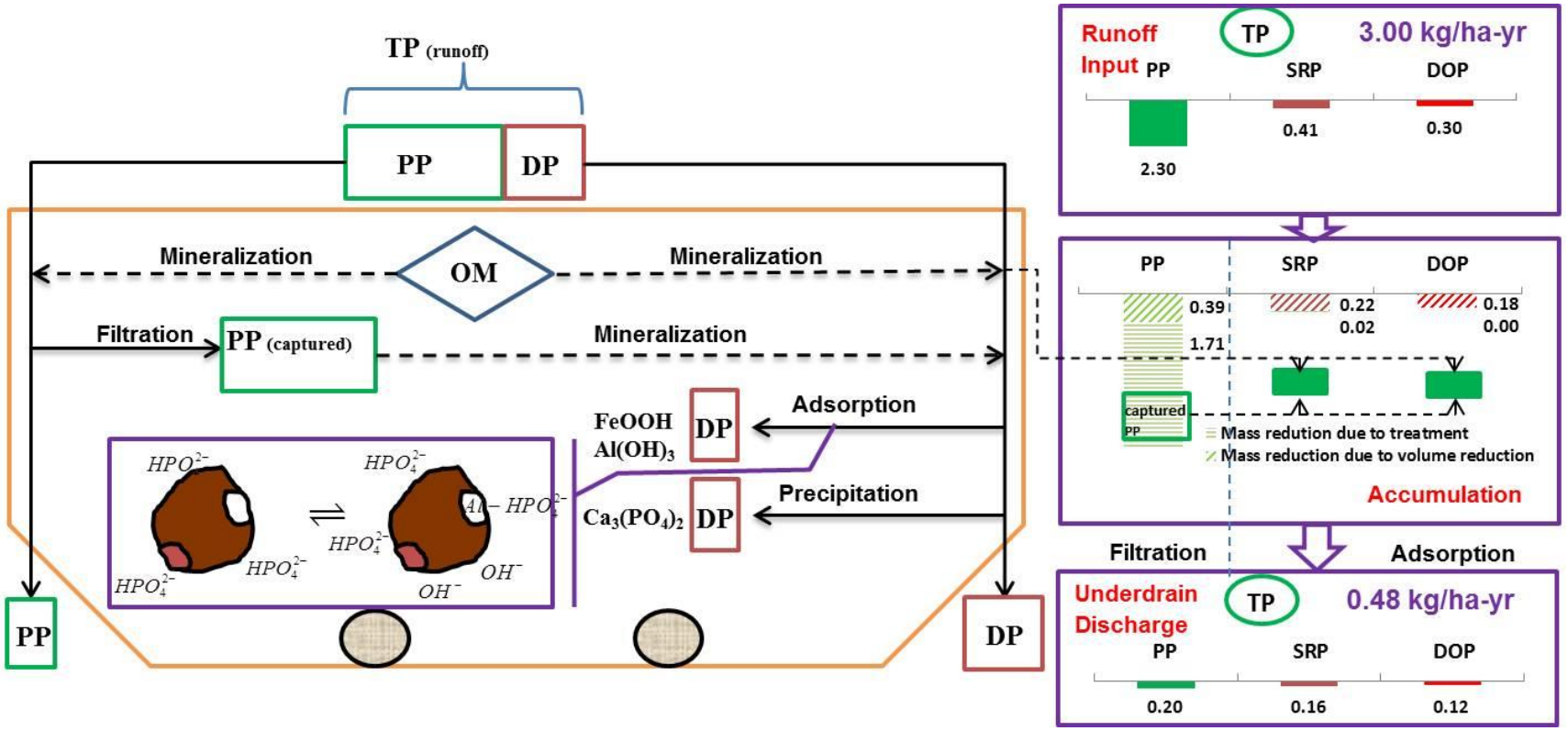


Figure 2-10 P fate in bioretention systems and pollutant mass loads: comparison between influent and effluent. (OM: organic matter).

2.4 Evidence and Limitations of Research

It has been proved by previous bench and column scale studies with restricted control and repetition experiments that WTR incorporation with bioretention media can greatly increase DP sorption capacity (O'Neill and Davis 2012b; O'Neill and Davis 2012a). Although no control and replicated treatments were able to be designed with this research, field study taken by Li (2007b) during 2006 – 2007 in the original bioretention system can be considered as a control experiment. Rainfall data collected in both monitoring periods (2006 - 2007, 2011 – 2013) were compared to the State of Maryland historical rainfall duration and depth (Kreeb 2003) and were recognized as typical Maryland storms. Moreover, the primary focus of this research is to evaluate the feasibility of this novel technology in a field complex environment. In order to simplify the research parameters, some assumptions were made: (i) data collected by Li (2007b) during 2006 – 2007 were still valid to just before the retrofit and were considered as control experiment data; (ii) the 5% WTR incorporation did not impact the results; and (iii) storm events were independent from each other.

TSS was significantly reduced by the bioretention cell for both the current and previous data periods, which is due to the settling and filtration prompted by the bioretention media (Li and Davis 2008b; Li and Davis 2008c). TP export was noted before WTR incorporation at this site (Li and Davis 2009), whereas TP was effectively managed after WTR retrofit. PP is managed with TSS (Davis 2007), exhibiting excellent removal in current study. Although no PP or DP data were collected in previous period (2006 - 2007), it can be assumed that the PP removal performance should have been good before the retrofit and the leaching of TP may

have resulted from leaching of DP, likely from organic matter in the media or captured PP by bioretention cell. Neither net removal nor leaching was indicated for both SRP and DOP from incoming runoff. Moreover the outflow concentrations were relatively stable, suggesting an adsorption mechanism.

Incorporation with WTR significantly increased the Al_{ox} and decreased the media PSI (described in Chapter 3), this is in accordance with the findings of O'Neill and Davis (2012a). PSI is often used to qualify P loss potential from a soil, and a critical value of 0.1 has been suggested for non-calcarious acidic to neutral soil systems (Agyin-Birikorang et al. 2009). Research has shown that a PSI > 0.1 greatly increases the risk of P leaching (Kleinman et al. 2000; Agyin-Birikorang and O'Connor 2007). The output EMCs (based on the cumulative mass divided by the cumulative volume for all collected samples) of SRP and DOP were identified as 0.037 mg/L and 0.028 mg/L, respectively. DOP accounts for 43% of DP, compared to the results of the leaching study described in Chapter 3, which found that $f_{d\text{-}org}$ = 67%, indicating that DOP was managed well by WTR addition, as well as SRP.

2.5 Summary

This project demonstrated the capacity of WTR incorporation within a traditional bioretention system to reduce stormwater volume, as well as TSS and P loads. The WTR incorporated into the bioretention system demonstrated excellent hydrologic performance. Although the field-determined BAV was lower than the calculated BAV, indicating that the bioretention cell was not fully utilized, volume reduction was noted for more than 96% of the monitored storm events. The input EMCs for TP and DP were 0.30 and 0.07 mg/L, respectively, which are close to the mean values

provided by USEPA (1999) for runoff from mixed urban areas: 0.26 and 0.06 mg/L. Results indicate good performance for TSS and P removal and reveal the following information on the unit processes of P removal in WTR-amended bioretention systems: (i) filtration performance was not harmed by WTR incorporation, and TSS, TP and PP were significantly reduced compared to input; and (ii) WTR incorporation can enhance the sorption capacity for both SRP and DOP, which can effectively treat incoming runoff and from media and prevent leaching from captured PP. Enhanced P removal through WTR appears to be a viable option for reducing uncertainty in design, decision making, and applications to address P removal from urban stormwater.

Chapter 3: Bioretention Retrofit for Enhanced Phosphorus Removal: Media Performance

3.1 Introduction

Phosphorus (P) can be the limiting nutrient in eutrophication processes, causing excessive phytoplankton growth and dissolved oxygen depletion in water bodies (Schindler 1977; Correll 1998). Although bioretention systems have been proven by many researches that they are effective at managing flows and volume, and a multitude of pollutants such as total suspended solids (TSS), hydrocarbons and heavy metals (Davis et al. 2001; Sóby et al. 2001; Davis 2007; Bratieres et al. 2008; Li and Davis 2008a; Li and Davis 2009; Trowsdale and Simcock 2011), they are generally not effective at addressing nutrients problems. P export from traditional bioretention media has been noted in several studies, which have concluded that high phosphorus content in the media was the cause of the total phosphorus (TP) export. In field research by Dietz and Clausen (2005a) in Haddam, CT and by Hunt et al. (2006) in Greensboro, NC, the mass retention for TP was found to be -110.6% and -240%, respectively, indicating more phosphorus left the system than entered. Li and Davis (2009) did field research on the campus of the University of Maryland, College Park, and found that the concentrations of total phosphorus (TP) in effluents were found higher than in influents.

Particulate phosphorus (PP) removal by traditional bioretention relies mainly on the filtration mechanism. Dissolved phosphorus (DP) can be retained in soil by

adsorption, which takes place both in static soil components and mobile sediments or colloids (McGechan and Lewis 2002). If the DP concentration exceeds the sorption capacity of the soil, the excess amount will dissolve and move freely with the water; eventually it will be transported to surface waters and possibly underground aquifers (Domagalski and Johnson 2012). As a result, the effectiveness of DP removal at traditional bioretention facilities can be highly variable, depending upon site-specific conditions.

The P sorption capacity of a soil depends upon its amorphous aluminum and iron content (Hsu 1964; Hsu 1965; Lijklema 1980; Elliott et al. 1990). Phosphate is adsorbed on the mineral oxide surface as binuclear bridging complexes by replacing hydroxyl groups (Parfitt 1979; Bohn et al. 1985).

Water treatment residuals (WTRs) are byproducts of municipal drinking water treatment plants that can be obtained either at a low cost or for free, which are high in aluminum (*Al* –) and/or iron (*Fe* –). The amorphous hydrous oxides in WTR have strong affinity for anionic species (Ippolito et al. 2011), which can help to increase the soil's P sorption capacity (Elliott et al. 1990).The hydrology and water quality performance of the University of Maryland WTR-enhanced P removal bioretention site were presented in Chapter 2. However, several questions remain to be clarified, such as: (i) What is the P distribution and movement during the running period of this WTR-amended bioretention site? (ii) Why did P leaching occur before the retrofit, and did the WTR addition really help to adsorb P in the media? and (iii) What is the P removal mechanism at this WTR-amended bioretention site?

3.2 Methodology

3.2.1 Site Description

The P1 site was described in section 2.2.1. The retrofit work began in April of 2011. The existing bioretention site was cleared of vegetation, except for the trees. Fifteen tons of aluminum-based WTR (wet weight) were obtained from the Rockville drinking water treatment plant in Potomac, Maryland, USA in May of 2011 and incorporated into the top 40 cm of the bioretention soil media (BSM) (Figure 3-1). The vegetation at this site was replanted in June of 2011. All the plants were selected on the basis of species status as native to the mid-Atlantic region of the United States, as shown in Table 3-1.

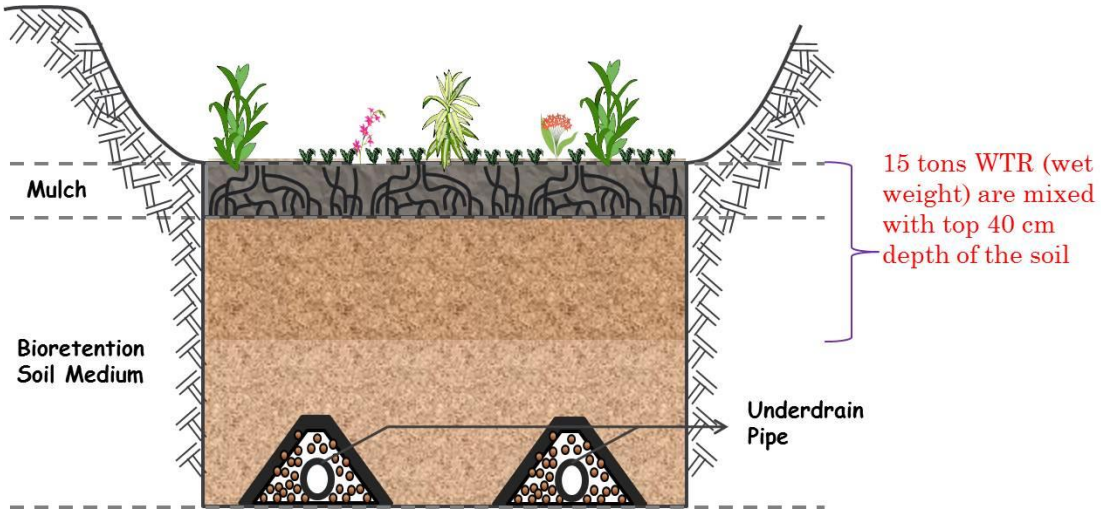


Figure 3-1 WTR retrofit at enhanced P removal bioretention site.

Table 3-1 Plant material at enhanced P removal bioretention site.

Herbaceous plants	
Scientific name	Common name
Carex pensylvanica	Pennsylvania sedge
Eupatorium dubium 'Little Joe'	Dwarf Joe Pye weed
Hibiscus x 'Lord Baltimore'	Lord Baltimore rose mallow
Panicum virgatum 'Cloud Nine'	Cloud nine switchgrass
Rudbeckia laciniata 'Goldquelle'	Cutleaf coneflower
Symphyotrichum novae-angliae *'Purple Dome'*	'Purple dome' aster
Woody plants	
Scientific name	Common name
Betula nigra 'BNMTF' Dura-Heat®	Dura Heat® river birch
Clethra alnifolia	Summersweet
Photinia pyrifolia 'Brilliantissima'	Red chokeberry

3.2.2 Monitoring and Sampling Methodology

Media Texture Study. Media samples were manually taken at May 21, 2013 at the narrow side of the P1 site in an area of approximately 10 m^2. Approximately 250 g sample was taken from the mixed sample of five cores and sent to the University of Delaware Soil Testing Program for characterization. Since P1 site was not fully used, stormwater runoff could not go as far to the narrow side. The sample was assumed to reflect the original condition of the P1site just after WTR retrofit.

Field Study. Media samples were collected in the P1 site five times, on April 26, 2011 (before the retrofit), August 31, 2011 (running two months), March 9, 2012 (running eight months), October 16, 2012 (running fifteen months) and March 1, 2013 (running twenty months). Four groups of media samples were collected along the mid line of the P1 site, moving from the wide side to the narrow side. 3-m intervals were maintained between the groups. Five cores were collected for each group over an area of 30 cm × 30 cm. Samples were taken from the top 24 cm of the

horizon and divided vertically into five samples, as follows: 2 cm / 2 cm / 4 cm / 4 cm / 12 cm. The five samples for each layer of each group were mixed together. As a result, 20 samples were obtained each time. The sampling schematic is shown in Figure 3-2.

Media samples were stored at field moisture content under refrigeration, between 0 and 4°C. Before testing, the media samples were crushed by hand, air dried for one week and passed through a No. 10 sieve (2 mm).

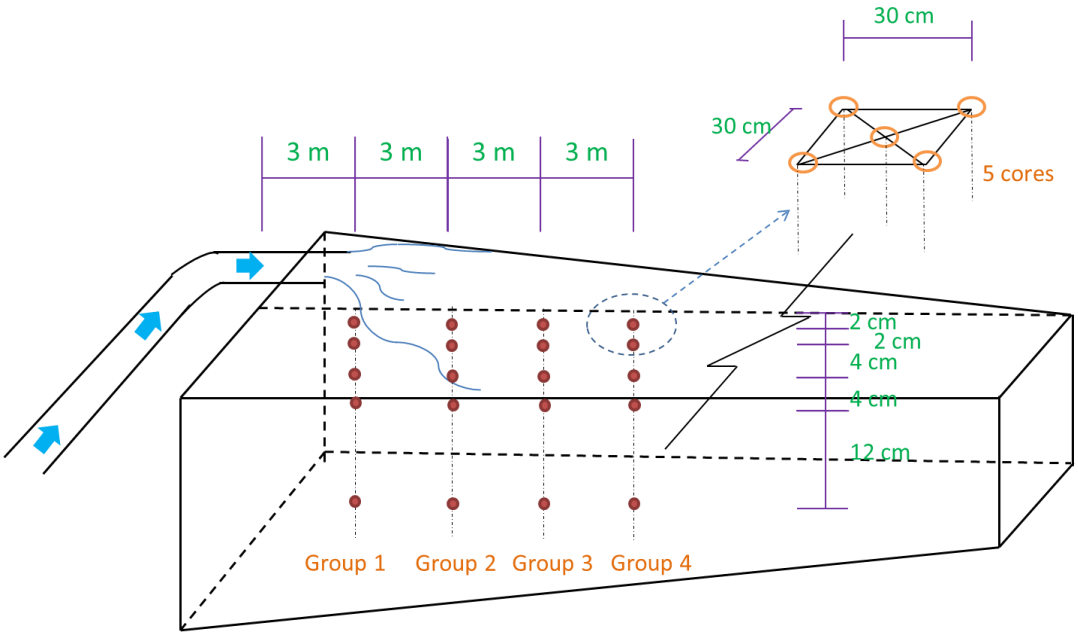


Figure 3-2 Media sampling schematic for enhanced P removal bioretention site.

Lab Study. TSS P leaching tests were conducted as follows. The first step was to collect first-flush stormwater influent at the P1 site during a storm, as described in Chapter 2. After taking a 100 mL sample for TP, TDP and SRP analysis, the remaining sample was filtered through a 0.22 μm membrane filter. The volume was recorded (V1) and the filter sample air dried at room temperature. For the second step,

after three days the filter was washed using DI water with the volume as recorded before (V1), and then the sample was shaken for one hour. Subsequently, after taking a 100 mL sample for TP, TDP and SRP analysis, the remaining sample was filtered through a 0.22 μm membrane filter. The volume was recorded (V2 = V1 - 100) and the filter sample air dried at room temperature. Finally, for the third step the second step was repeated until the sample volume was less than 100 mL.

3.2.3 Analytical Procedures

The procedures used for determination of the water quality parameters were described in Section 2.2.3. The media parameters analyzed included pH, electrical conductance (EC), organic matter (OM), oxalate extractable Al (Al_{ox}), Fe (Fe_{ox}) and P (P_{ox}), water extractable P (WEP) and Mehlich 3 P (M3P).

A glass electrode probe pH meter (Mettler Toledo MA235, Greifensee, Switzerland) measured the pH of media and water mixtures (1:2 w/v). EC was determined by a conductance probe (YSI Model 35, Yellow Springs, Ohio) in a saturated media paste (1:1 w/v). OM content was estimated by loss-on-ignition (LOI) at 550°C.

WEP and M3P were analyzed using the method of Kovar and Pierzynski (2009). For WEP, media were extracted using 0.01 M CaCl at a w/v ratio of 1:25, shaking on a reciprocating shaker for one hour. For M3P, media were extracted by a Mehlich 3 extraction solution (0.2 M acetic acid + 0.25 M ammonium nitrite + 0.015 ammonium fluoride + 0.013 M nitric acid + 0.001 M EDTA) at a 1:10 (w/v) ratio and shaken on a reciprocating shaker for five minutes. Then both samples were

centrifuged at 4,000 rpm for 10 minutes and passed through a 0.22 μm membrane filter. The filtrates were tested spectrophotometrically using the ascorbic acid molybdenum blue method (4500-P E)(APHA 2005) at 880 nm (Shimadzu UV-160, Kyoto, Japan).

Media oxalate extractions were performed as described in McKeague and Day (1993). A 1 g media sample was placed in a 50 mL centrifuge tube along with 40 mL of 0.275 M extraction solution (0.175 M ammonium oxalate monohydrate + 0.1 M oxalic acid dehydrate, adjusted to pH = 3.0±0.1 with 1M HCl). The samples were shaken for two hours in the dark, centrifuged at 2,000 rpm for 13 minutes, and then filtered through 0.22 μm membrane filters. The filtrates were analyzed for Al, Fe and P within one week. Al and Fe were analyzed by Atomic Absorption Spectrophotometry (Perkin-Elmer 5100ZL, Waltham, Massachusetts). The P was analyzed spectrophotometrically by a spectrophotometer (Shimadzu, UV-160) at 660 nm, using the method described in Wolf and Baker (1990).

Scanning electron microscopy (SEM) (FEG-SEM, Hitachi SU-70, Japan) and Fourier Transform Infrared Spectroscopy (FT-IR) (Thermo Scientific, Nicolet 6700) with smart iTR attenuated total reflectance (ATR) sampling accessory were performed for WTR for morphology analysis.

3.2.4 Data Handling and Statistical Analyses

A strong correlation exists between oxalate extractable aluminum, iron ($Al_{ox} + Fe_{ox}$) and phosphorus (P_{ox}) in soil materials (McLaughlin et al. 1981). The

phosphorus saturation index (PSI) is defined (McGechan and Lewis 2002; Dayton and Basta 2005b):

$$PSI = \frac{P_{ox}}{Al_{ox} + Fe_{ox}}$$

Equation 3-1

where P_{ox}, Al_{ox} and Fe_{ox} are expressed on a molar basis (mmol/kg soil). PSI is often used to qualify P loss potential from a soil, and a critical value of 0.1 has been suggested for noncalcarious acidic to neutral soil systems (Agyin-Birikorang et al. 2009). Research has shown that a PSI > 0.1 greatly increases the risk of P leaching (Kleinman et al. 2000; Agyin-Birikorang and O'Connor 2007). PSI values were calculated for the bioretention media samples before the P1 site retrofit and every four to six months thereafter in order to determine if the WTR application resulted in P losses or sustained increases in the P sorptive capacity of the bioretention system.

One way ANOVA tests were used to determine if the addition of oxalate extractable contents (P_{ox}, Al_{ox} and Fe_{ox}) in soil media were statistically significant.

3.3 Results and Discussion

3.3.1 WTR Characterization

The basic characteristics of WTR are presented in Table 3-2. WTR is essentially neutral, with a pH of 6.5. The high apparent OM (36%) of WTR given by LOI is likely due to the chemical-bound water removed from the hydrous oxides of WTR during ignition (Elliott et al. 2002) or the nonionic organic polymer (CLARIFLOC N-6310 POLYMER) used in the drinking water coagulation processes

(O'Neill and Davis 2012a). The amount of amorphous Al and Fe (Al_{ox} + Fe_{ox}) was high and WEP was low, which implies the high sorption capacity and low leaching potential of P (McLaughlin et al. 1981; Elliott et al. 2002).WTR can be found in various shapes and sizes and is highly porous (Figure 3-3). Several peaks are apparent in the FT-IR patterns of WTR (Figure 3-4); however, since WTRs are physical mixtures of aluminum and iron hydrolysate (oxides) containing small quantities of activated carbon and polymer (Ren et al. 2013). It is difficult to clearly confirm the compositions at these peaks, however, the wavelength at around 3300 cm^{-1} should indicate hydroxyl groups; the two peaks at approximate wavelengths of 1400 cm^{-1} and 1600 cm^{-1} may due to the organic impurities; metal oxides, such as silica dioxide, aluminum oxide and iron oxide should contribute to the peak at the wavelength around 1000 cm^{-1}.

Table 3-2 WTR characteristics.

Characteristics	Values
pH	6.5
EC (mmohs/cm)	1.34
WC [moist] (%)	84.1
WC [air dry] (%)	15.6
LOI (%)*	36
Al_{ox} (g/kg)	123
Fe_{ox} (g/kg)	3.54
P_{ox} (g/kg)	0.469
WEP (mg/kg)	< 0.1
M3P (mg/kg)	2.03
PSI	0.003

* This value is likely not representative of the organic matter content due to the presence of bound water. See text for discussion.

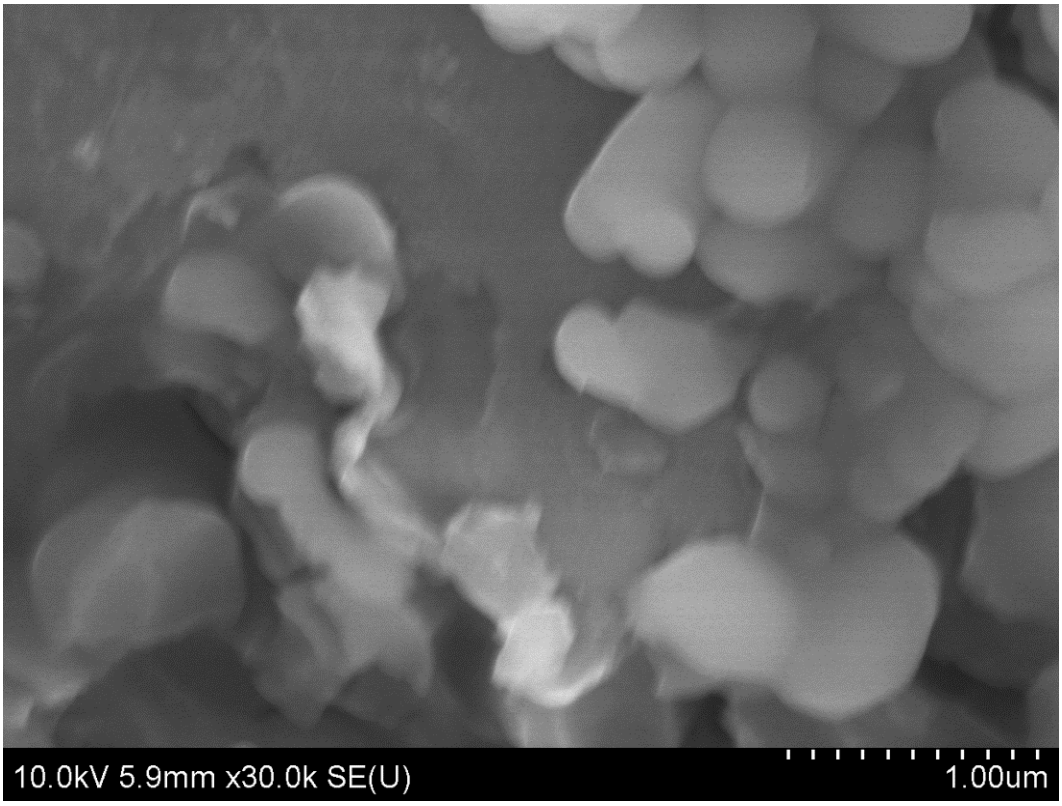


Figure 3-3 Scanning electron microscope image of an Al-WTR.

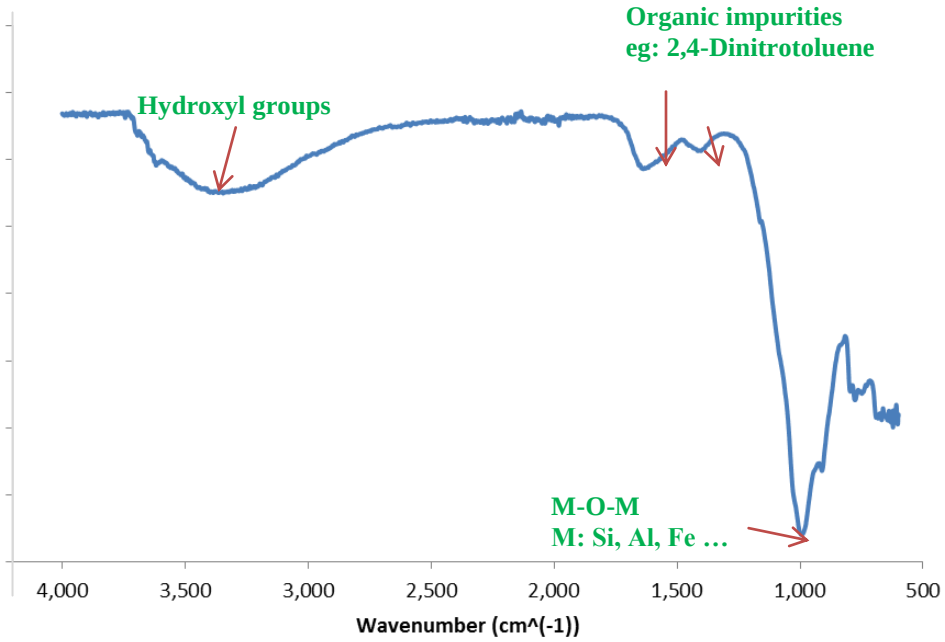


Figure 3-4 FT-IR patterns of WTR.

The results of the characterization studies performed by the Delaware Soil Testing Program before and after the retrofit are shown in Table 3-3. The soil texture did not change after the WTR retrofit; however, the pH decreased slightly from 7.3 to 6.8. WTR may also alter the pH of soils after addition. Increases in pH can decrease Al solubility in the short term. Also, decreases in pH can result in Al release (Figure 3-5). Generally, previous research on WTR has indicated that Al solubility does not increase when WTR is applied to soil (Peters and Basta 1996; Gallimore et al. 1999; Agyin-Birikorang et al. 2009). Davis et al. (2006) found that pH changes resulted in a phosphorus release in the upper soil media portion of the bioretention system (but did not affect the outflow phosphorus concentrations) due to the runoff buffering occurring within the soil depth.

Table 3-3 Media characterization of the P1 site before and after the WTR retrofit.

Characteristics	Before retrofit[a]	After retrofit
pH	7.3	6.8
Organic content (%)	5.7	5.1
Sand (%)	80	82
Silt (%)	13	10
Clay (%)	7	8
Soil Texture	Loamy Sand	Loamy Sand

[a]Data were collected by Li (2007b)

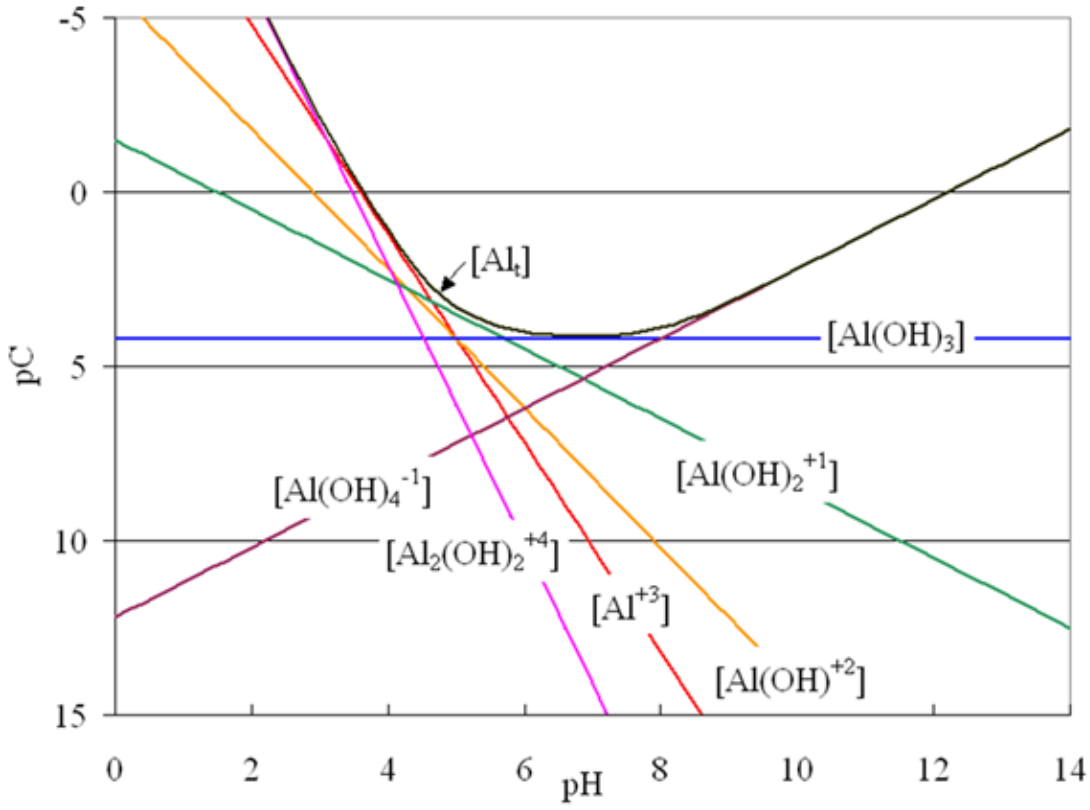


Figure 3-5 Solubility diagram for Aluminum (III) hydroxide (http://ceeserver.cee.cornell.edu/mw24/projects/SSF/alsol/aluminumsolubility.htm).

3.3.2 General Trends of Media Oxalate Extractions

Changes in media oxalate extractions, along with site depth, flow path, and time passage were investigated from before retrofit and during the entire running period. The oxalate-extractable contents and PSI values for the media samples are listed in Table 3-4. One way ANOVA tests were used to determine if the WTR addition increased oxalate extractable contents of P, Al and Fe.

Table 3-4 Summary of oxalate extractable contents and PSI collected at the enhanced P removal bioretention site for all samples and all depths

	P_{ox}	Al_{ox}	Fe_{ox}	PSI
	mmol/kg	mmol/kg	mmol/kg	
April 26, 2011	3.16 ± 0.59	10.80 ± 3.01	33.95 ± 5.91	0.075 ± 0.003
August 31, 2011	3.27 ± 0.80	64.74 ± 21.46	22.46 ± 2.26	0.048 ± 0.004
March 12, 2012	3.62 ± 0.37	92.92 ± 9.36	23.97 ± 2.67	0.031 ± 0.001
October 16, 2012	4.02 ± 0.27	69.92 ± 5.77	22.02 ± 1.39	0.045 ± 0.002
March 1, 2013	4.20 ± 0.63	80.10 ± 12.77	28.40 ± 4.27	0.039 ± 0.001

Figure 3-6 shows the values of the media samples collected at the P1 site before the WTR retrofit. At that time, the P1 site had been running as a traditional bioretention site for seven years. P_{ox}, Al_{ox} and Fe_{ox} were found to accumulate in the top 4 cm of the media. This investigation is in accordance with the results of Sharpley (1985), which concluded that the effective depth of interaction between surface soil and runoff ranged from 2 to 40 mm (Komlos and Traver 2012). In the same layer, group 2 has the highest concentrations of media oxalate extractions elements (From Figure 3-2, since the flume inlet, which extended 40 cm into P1 site, is close to a long side of the trapezoid, group 2 media was more likely to be exposed to runoff during the storm events due to the flow pathway). The values of all the P_{ox}, Al_{ox} and Fe_{ox} decreased following the inflow pathway: group 2 > group 1 ~ group 3 > group 4 (top media). The average PSI was 0.075, indicating a low P leaching risk (Agyin-Birikorang et al. 2009). However, the PSI values increased as the media got deeper. The lower PSI values in the top media, is due to the accumulation of amorphous Al and Fe as seen, which can reinforce the P sorption ability of media (Elliott et al. 2002; Agyin-Birikorang and O'Connor 2007).

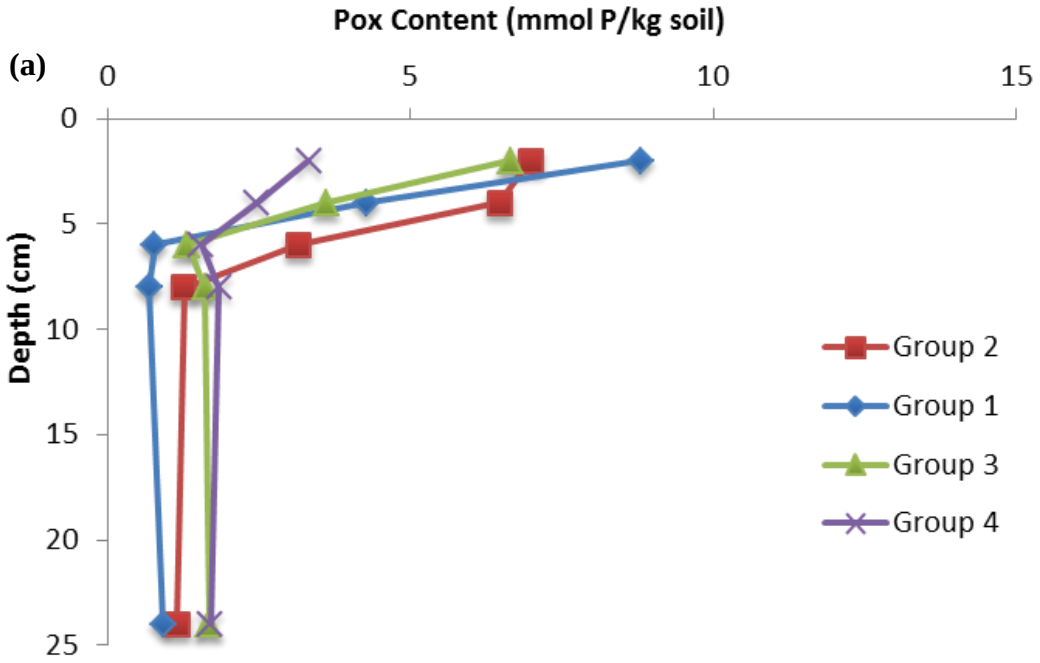
The highest P_{ox}, Al_{ox} and Fe_{ox} media moved from the surface soil (0 – 4 cm) to 8-12 cm after the retrofit (Figure 3-7). This is likely because the mixing of the WTR into the media moved the former topsoil to a lower location. Based on the WTR characteristics in **Error! Reference source not found.**, the expected increases of P_{ox}, Al_{ox} and Fe_{ox} concentrations were 0.41 mmol/kg, 124 mmol/kg and 1.7 mmol/kg, respectively due to the WTR incorporation. Comparing the mean values on April 26, 2011 (before retrofit) and August 31, 2011 (after retrofit), the addition of P_{ox} and Fe_{ox} was not obvious, which is attributed to the high variability among samples. The mean PSI was 0.048, reduced significantly from the mean value of 0.075 before the retrofit, which means the P loss potential was very low after the WTR application. However, differences of PSI values were found not only between different layers but also between different groups, which may be have resulted from uneven mixing of WTR with the BSM.

With continued operation, P_{ox} again accumulated in the top media (Figure 3-8, Figure 3-9 and Figure 3-10). Unlike before the retrofit where P was only retained in the surface media, after the retrofit P was able to be adsorbed by the lower media (the average values of P_{ox} at the depth of 4 – 24 cm after retrofit were all higher than the values at April 26, 2011, which may be due to the retrofit mixing). The layer and group average values with standard error are shown in Figure 3-11 and Figure 3-12. The gradient of oxalate extractions concentrations for groups did not vary a lot. Group 2 still was the group with highest concentrations of oxalate extractable of P, Al and Fe, due to the fact that it received more runoff during storm events. Fe_{ox} did not significantly increase after the retrofit, but the vertical distribution was much more

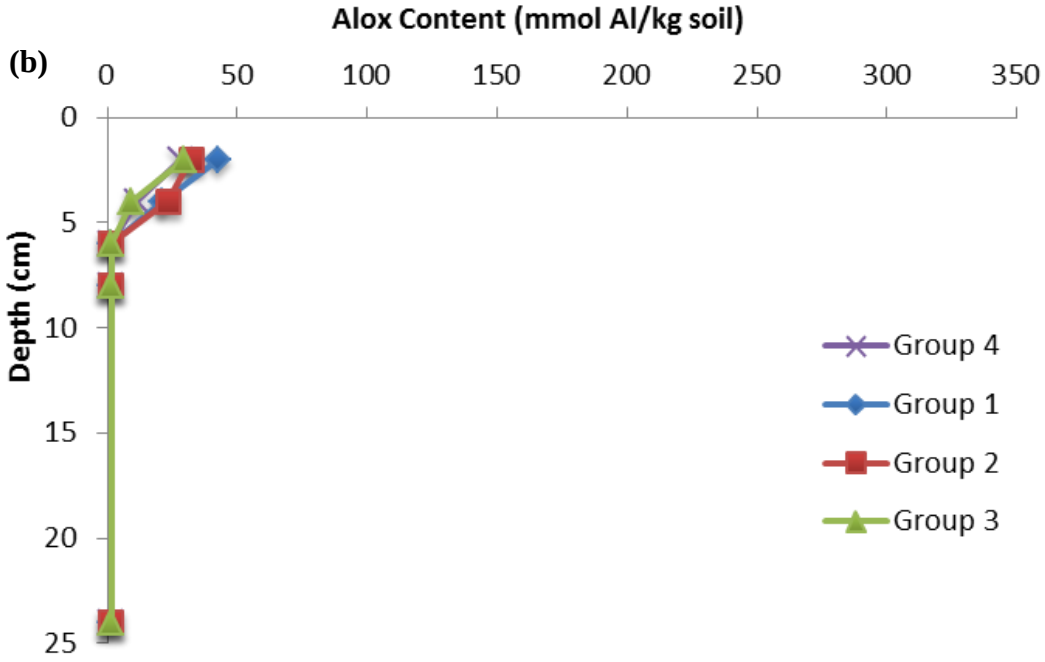
even than it was before the retrofit. Even though the Al_{ox} values varied a lot after WTR addition, all values were all higher than before the retrofit. The extremely high value of August, 2011 could be because the core sample contained much more WTR. Since this is a field project, the WTR could not be completely mixed with BSM. PSI values changed only minimally and always remained below 0.05 after the retrofit, indicating that the WTR amendment continued to work well after two years in operation.

One way ANOVA tests indicated that the addition of amorphous Al and the increased of P adsorption capacity of the soil median were statistical significant. This resulted from the WTR addition and was in accordance with the findings of O'Neill and Davis (2012a). An increase in the $Fe_{ox} + Al_{ox}$ content of the WTR-amended media was expected to increase the P sorption capacity of the soil.

(a)


Pox Content (mmol P/kg soil)
0
5
10
15
Depth (cm)
0
5
10
15
20
25
Group 2
Group 1
Group 3
Group 4

(b)


Alox Content (mmol Al/kg soil)
0
50
100
150
200
250
300
350
Depth (cm)
0
5
10
15
20
25
Group 4
Group 1
Group 2
Group 3

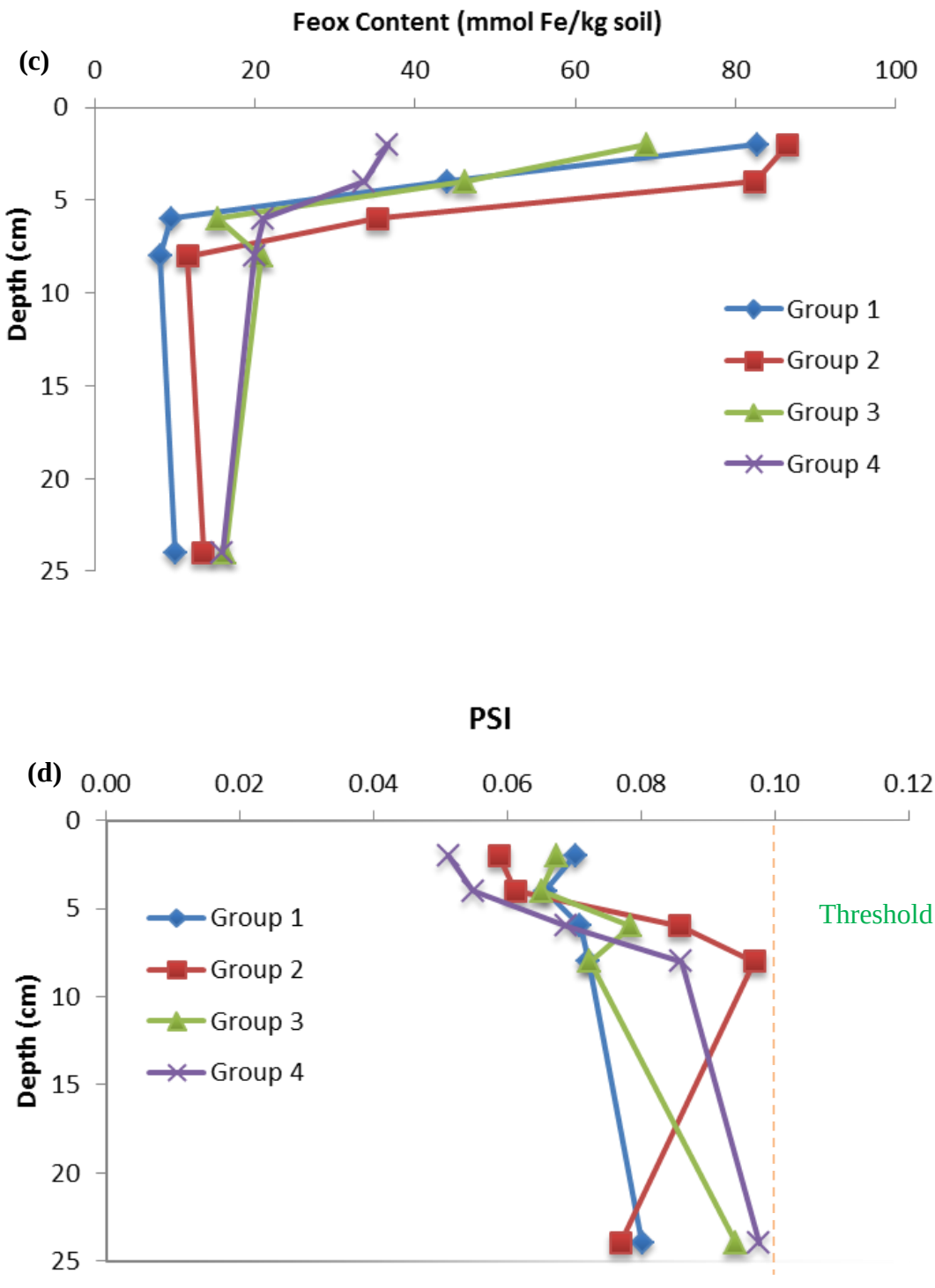
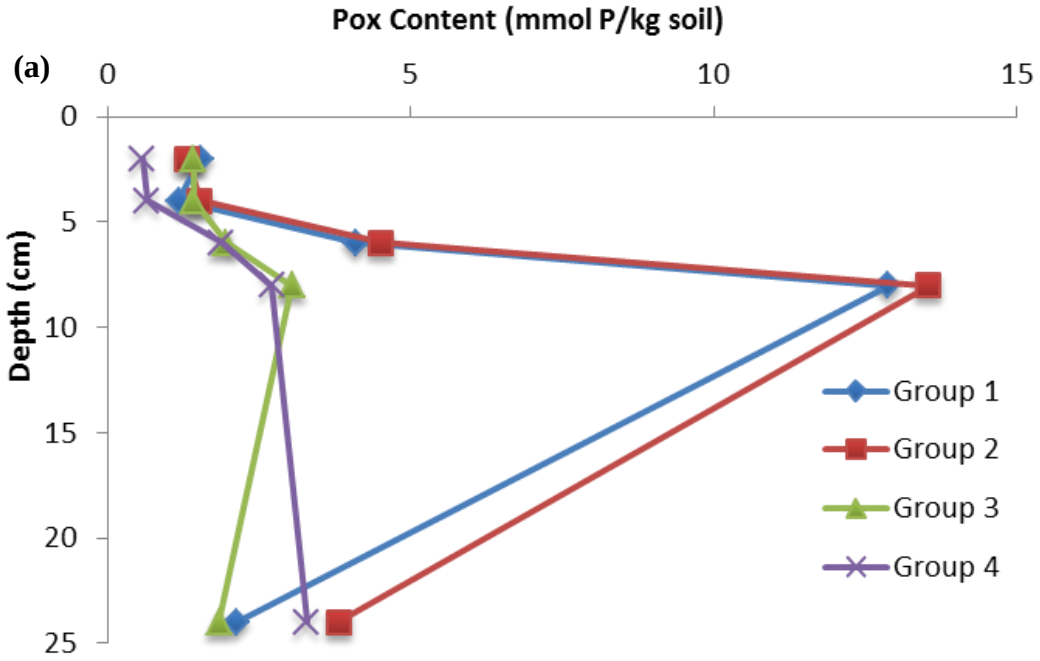
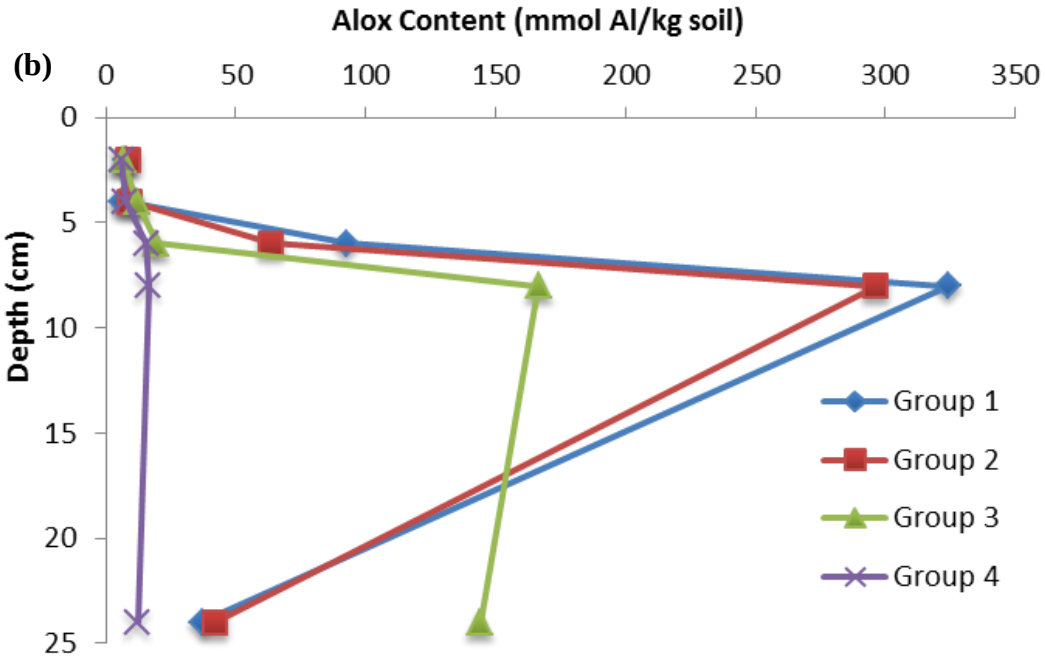


Figure 3-6 Oxalate extractable contents and PSI collected at enhanced P removal bioretention site at April 26, 2011: (a) P_{ox}; (b) Al_{ox}; (c) Fe_{ox}; (d) PSI.

(a)


Pox Content (mmol P/kg soil)
0
5
10
15
Depth (cm)
0
5
10
15
20
25
Group 1
Group 2
Group 3
Group 4

(b)


Alox Content (mmol Al/kg soil)
0
50
100
150
200
250
300
350
Depth (cm)
0
5
10
15
20
25
Group 1
Group 2
Group 3
Group 4

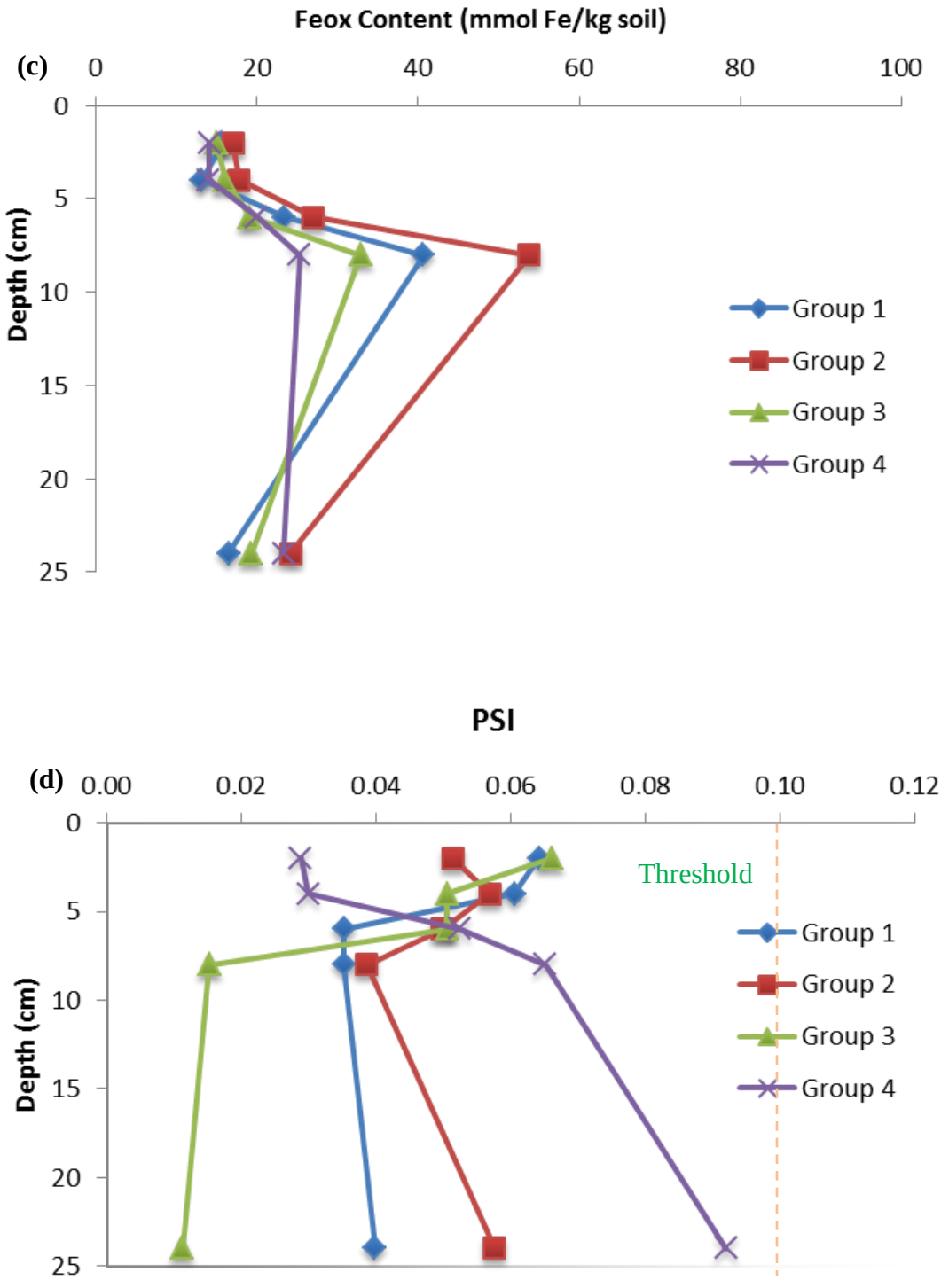
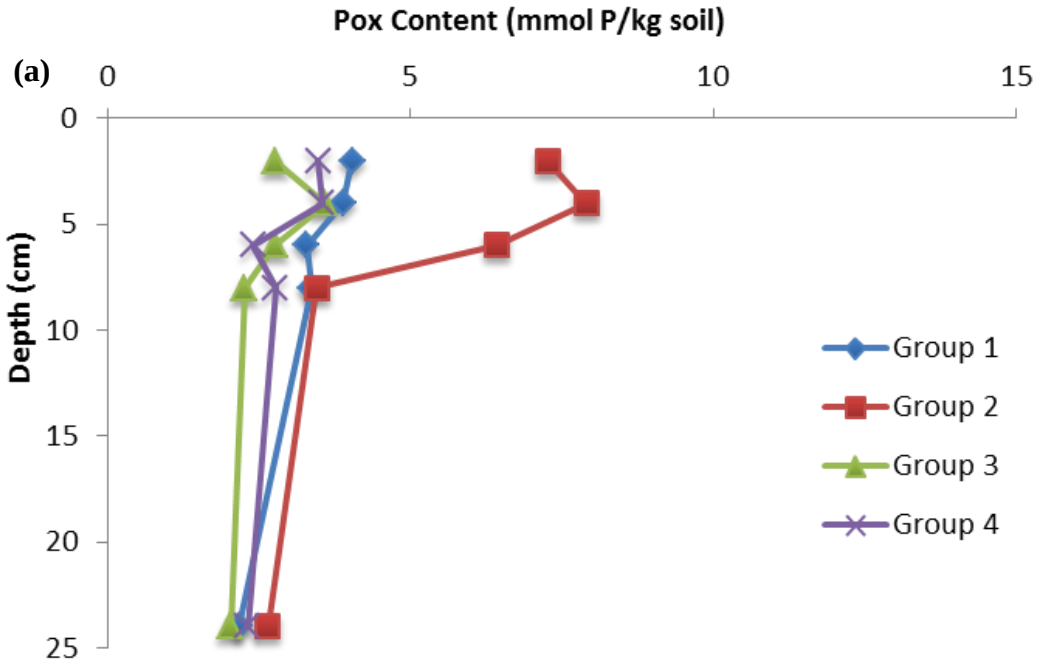
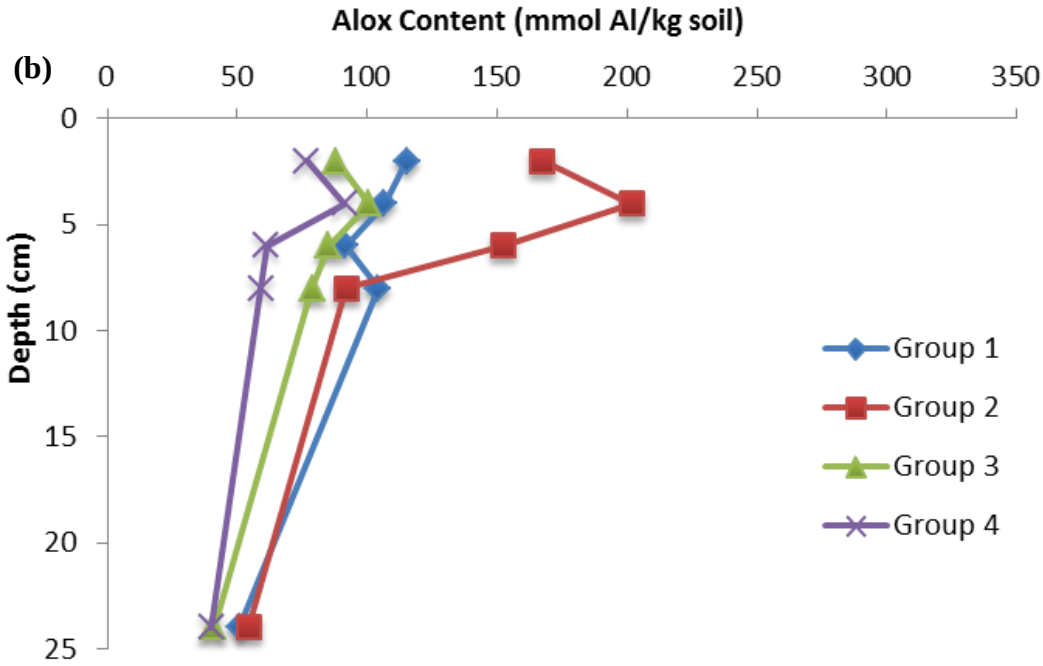


Figure 3-7 Oxalate extractable contents and PSI collected at enhanced P removal bioretention site at August 31, 2011: (a) P_{ox}; (b) Al_{ox}; (c) Fe_{ox}; (d) PSI.


(a)
Pox Content (mmol P/kg soil)
0
5
10
15
Depth (cm)
0
5
10
15
20
25
Group 1
Group 2
Group 3
Group 4


(b)
Alox Content (mmol Al/kg soil)
0
50
100
150
200
250
300
350
Depth (cm)
0
5
10
15
20
25
Group 1
Group 2
Group 3
Group 4

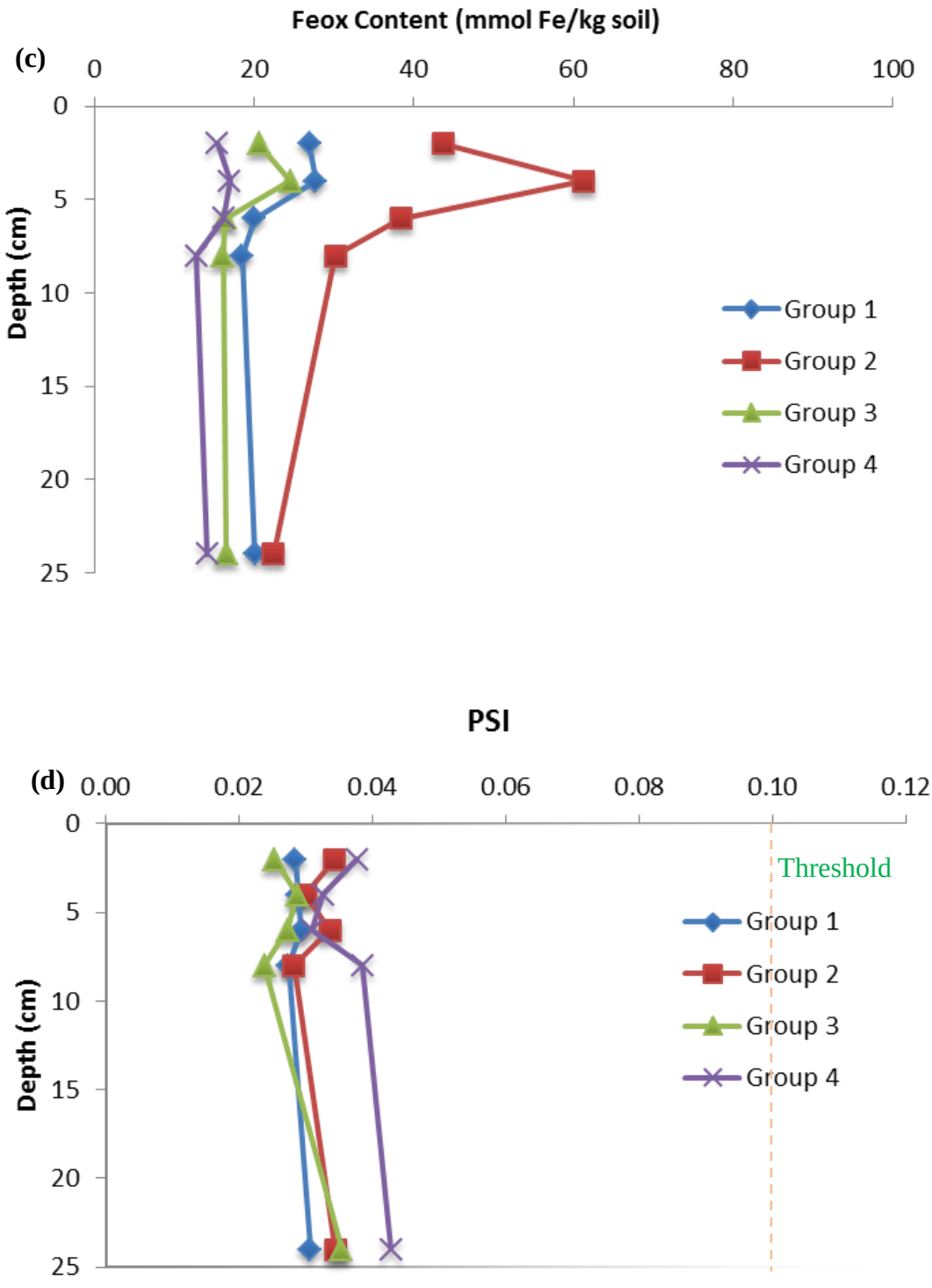
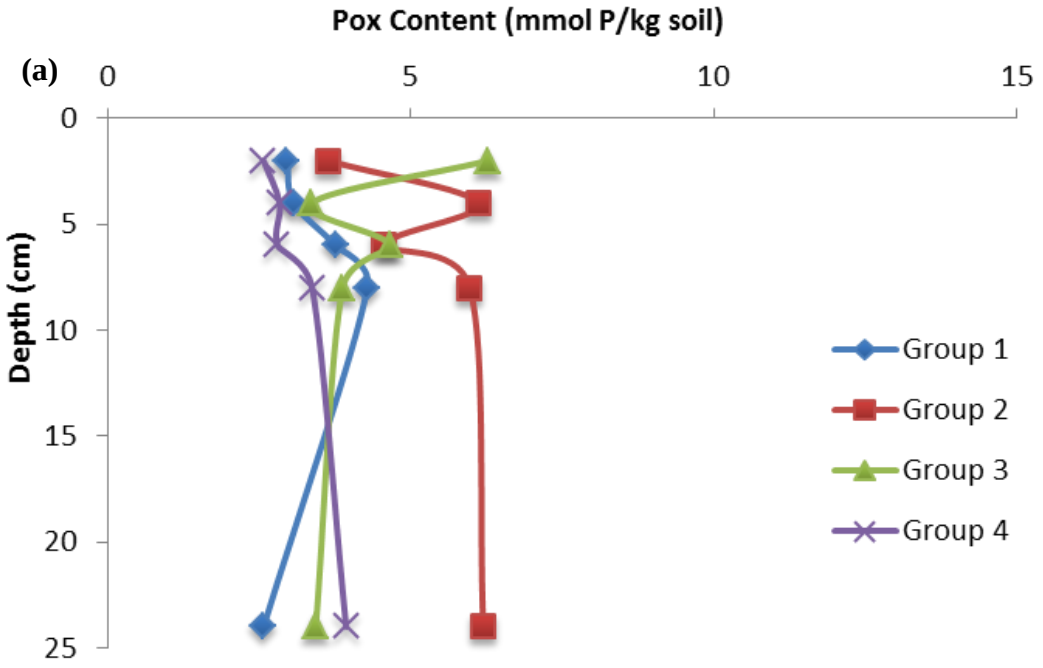
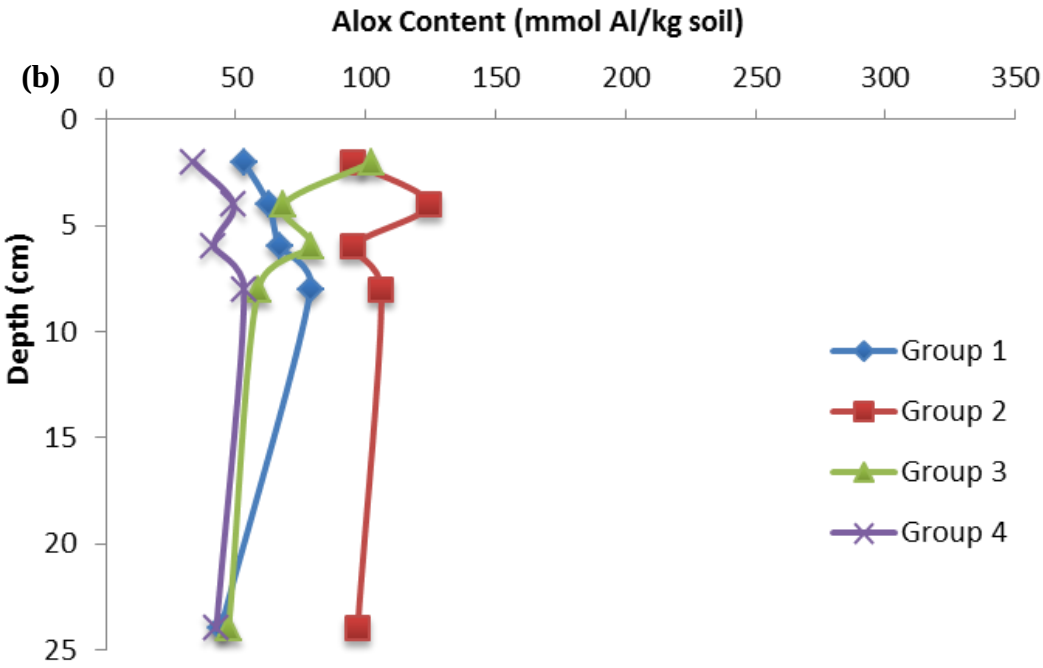


Figure 3-8 Oxalate extractable contents and PSI collected at enhanced P removal bioretention site at March 9, 2012: (a) P_{ox}; (b) Al_{ox}; (c) Fe_{ox}; (d) PSI.


(a)
Pox Content (mmol P/kg soil)
0
5
10
15
Depth (cm)
0
5
10
15
20
25
Group 1
Group 2
Group 3
Group 4


(b)
Alox Content (mmol Al/kg soil)
0
50
100
150
200
250
300
350
Depth (cm)
0
5
10
15
20
25
Group 1
Group 2
Group 3
Group 4

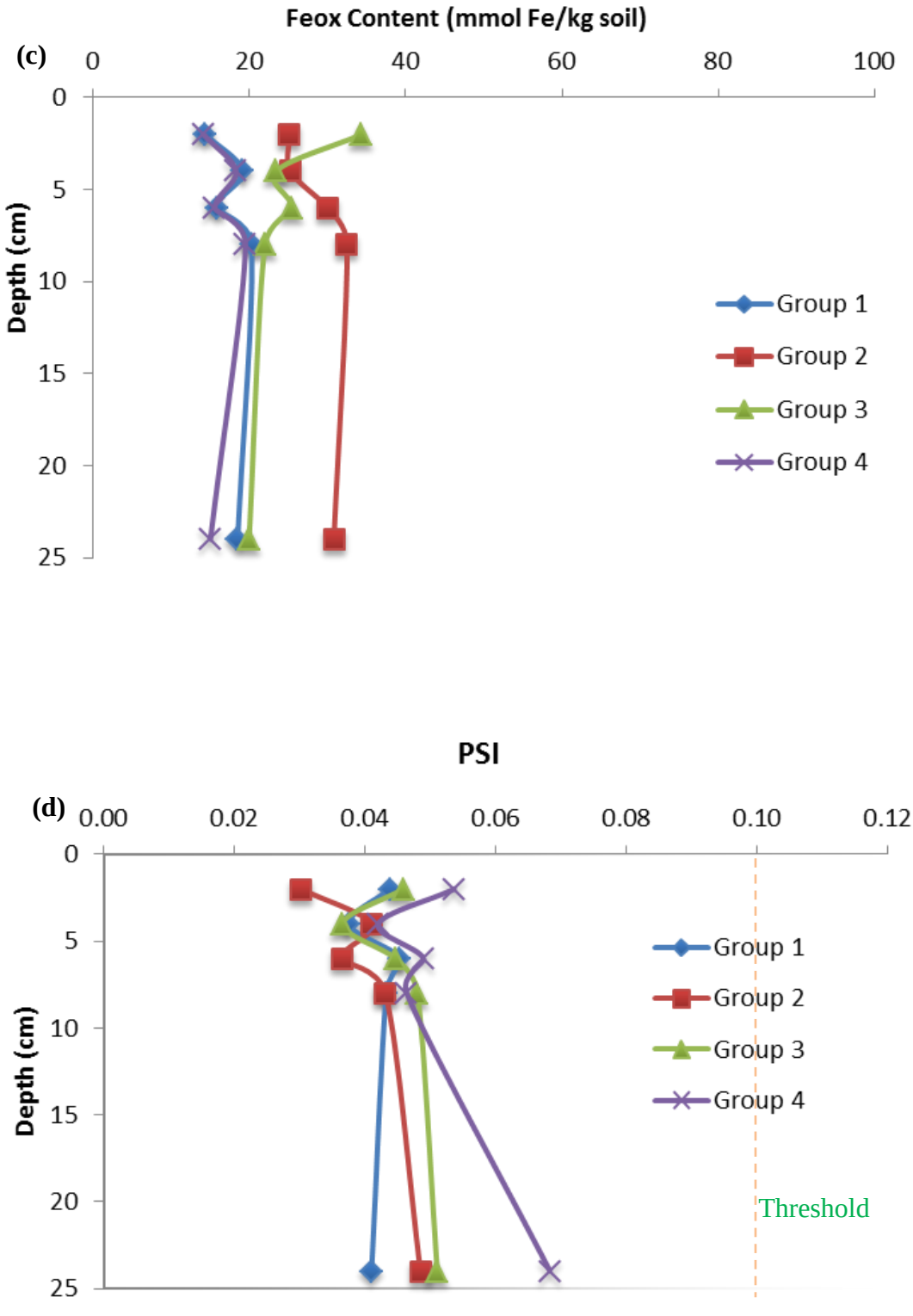
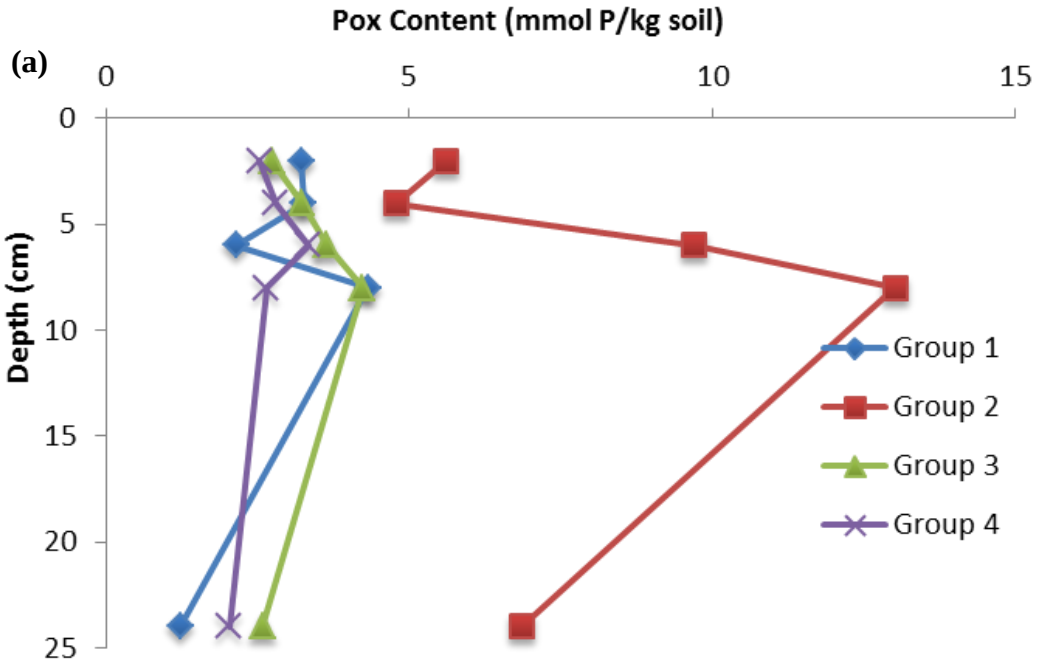
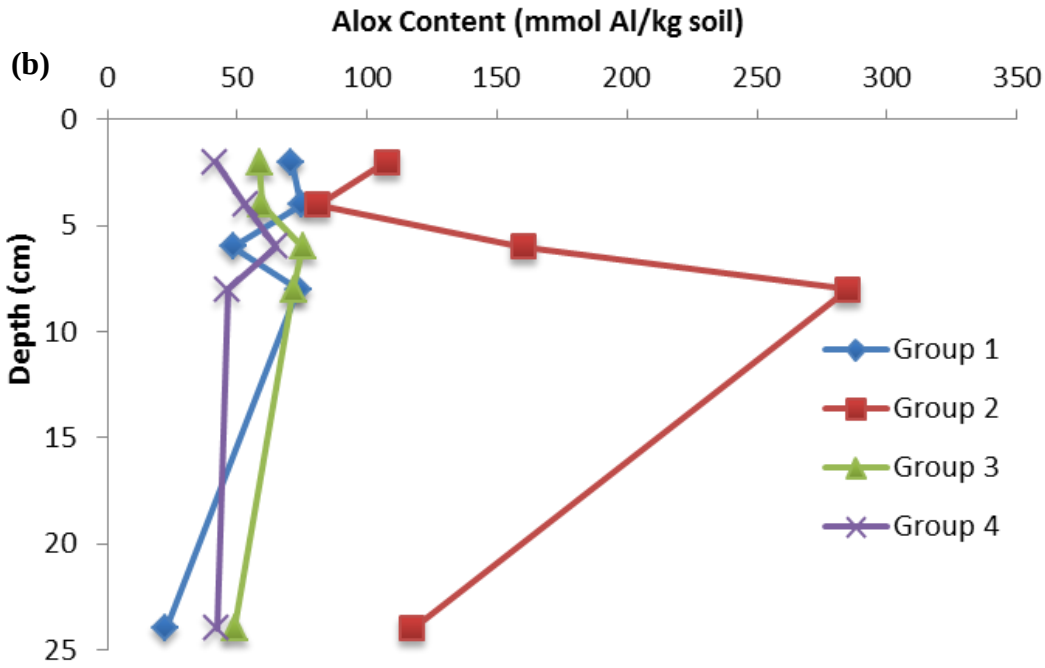


Figure 3-9 Oxalate extractable contents and PSI collected at enhanced P removal bioretention site at October 16, 2012: (a) P_{ox}; (b) Al_{ox}; (c) Fe_{ox}; (d) PSI.


(a)
Pox Content (mmol P/kg soil)
0
5
10
15
Depth (cm)
0
5
10
15
20
25
Group 1
Group 2
Group 3
Group 4


(b)
Alox Content (mmol Al/kg soil)
0
50
100
150
200
250
300
350
Depth (cm)
0
5
10
15
20
25
Group 1
Group 2
Group 3
Group 4

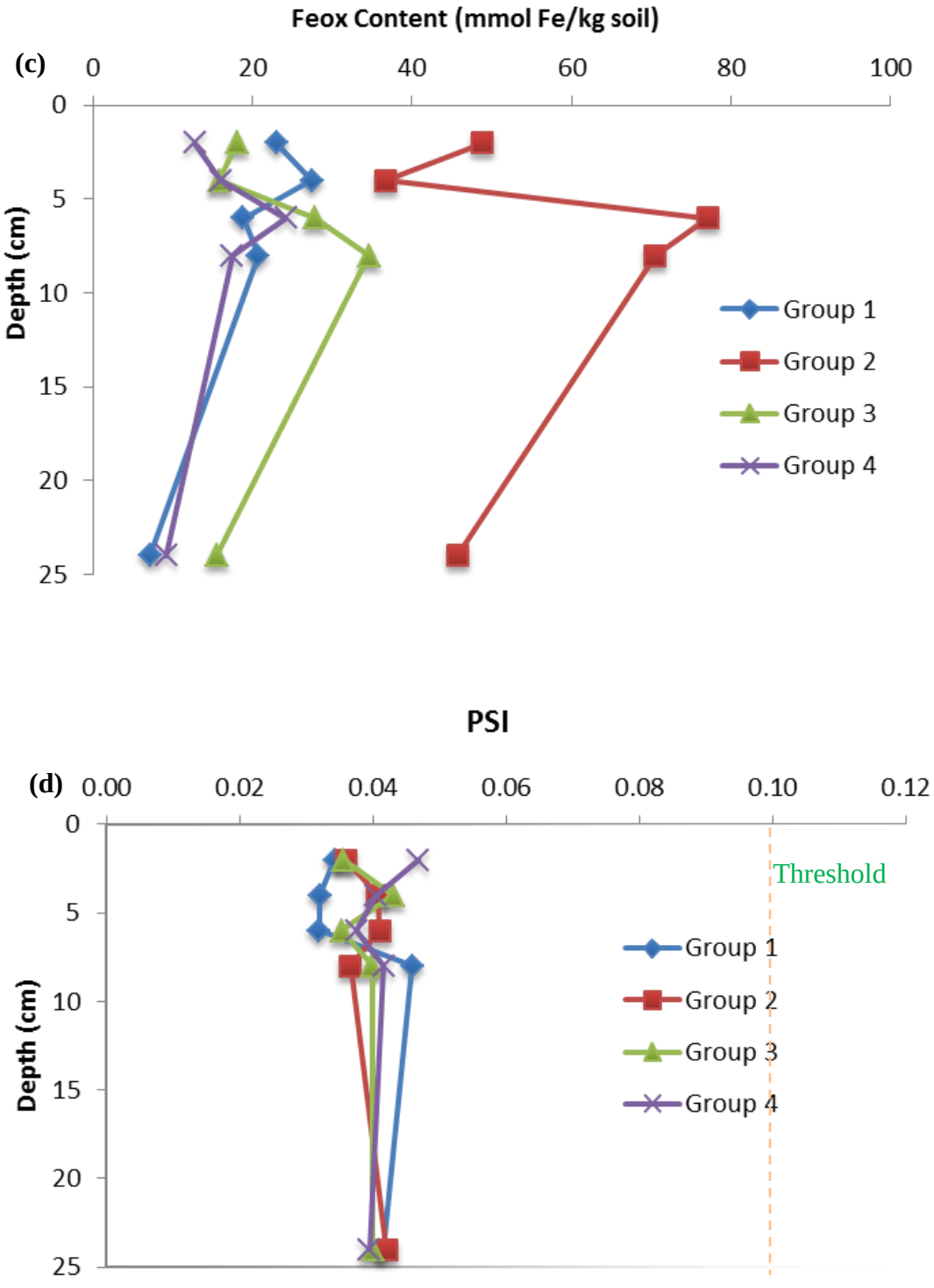
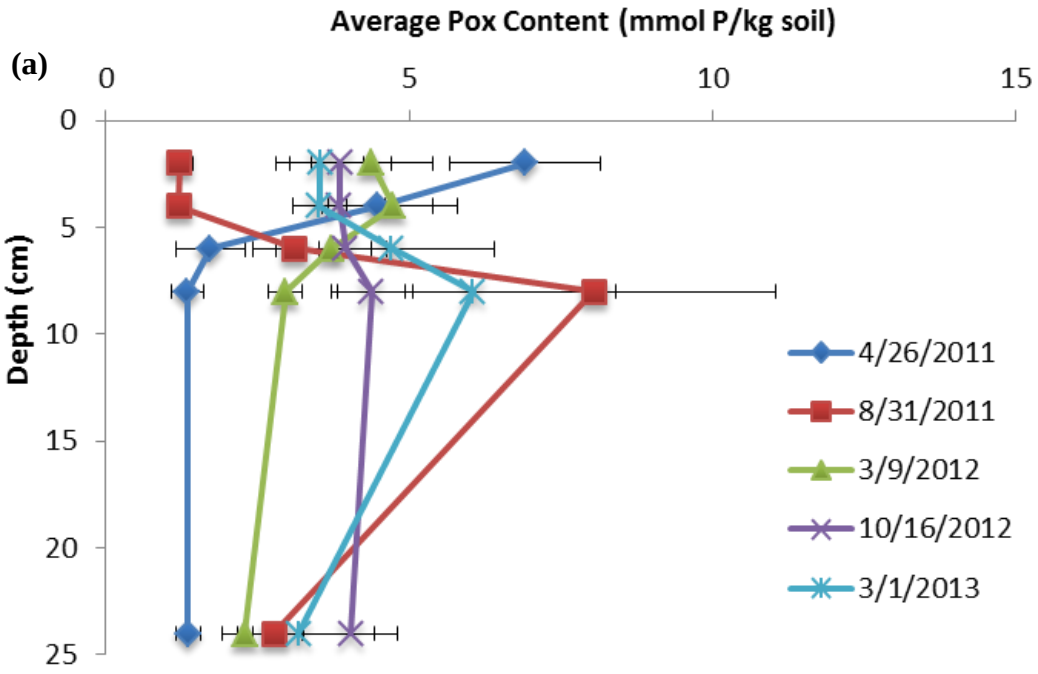
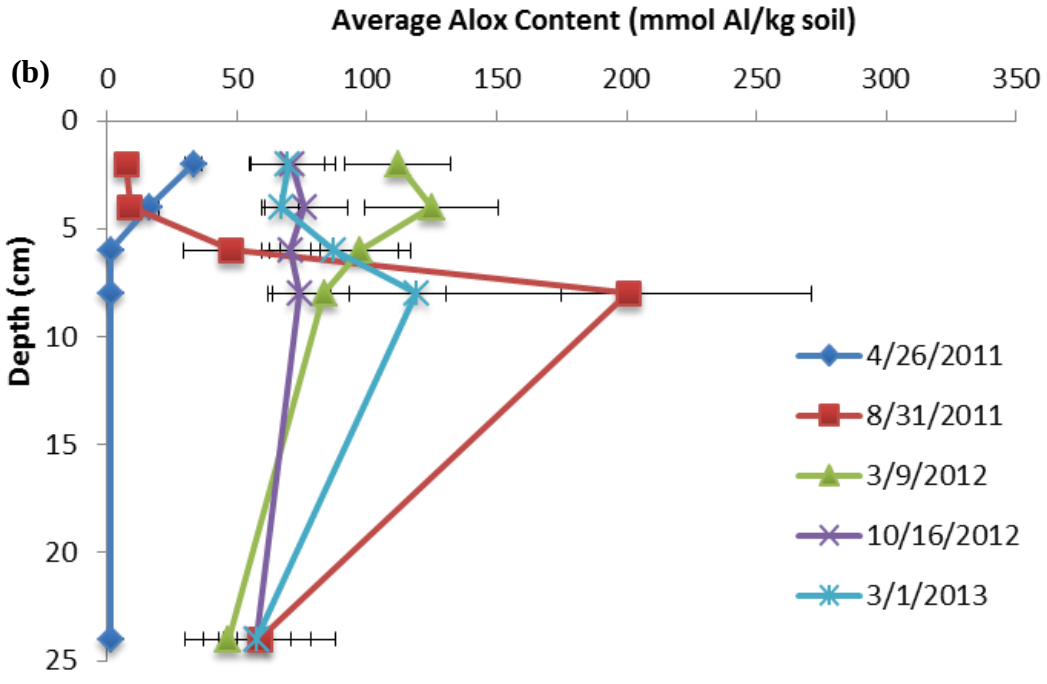


Figure 3-10 Oxalate extractable contents and PSI collected at enhanced P removal bioretention site at March 1, 2013: (a) P_{ox}; (b) Al_{ox}; (c) Fe_{ox}; (d) PSI.


(a)
Average Pox Content (mmol P/kg soil)
0
5
10
15
Depth (cm)
0
5
10
15
20
25
4/26/2011
8/31/2011
3/9/2012
10/16/2012
3/1/2013


(b)
Average Alox Content (mmol Al/kg soil)
0
50
100
150
200
250
300
350
Depth (cm)
0
5
10
15
20
25
4/26/2011
8/31/2011
3/9/2012
10/16/2012
3/1/2013

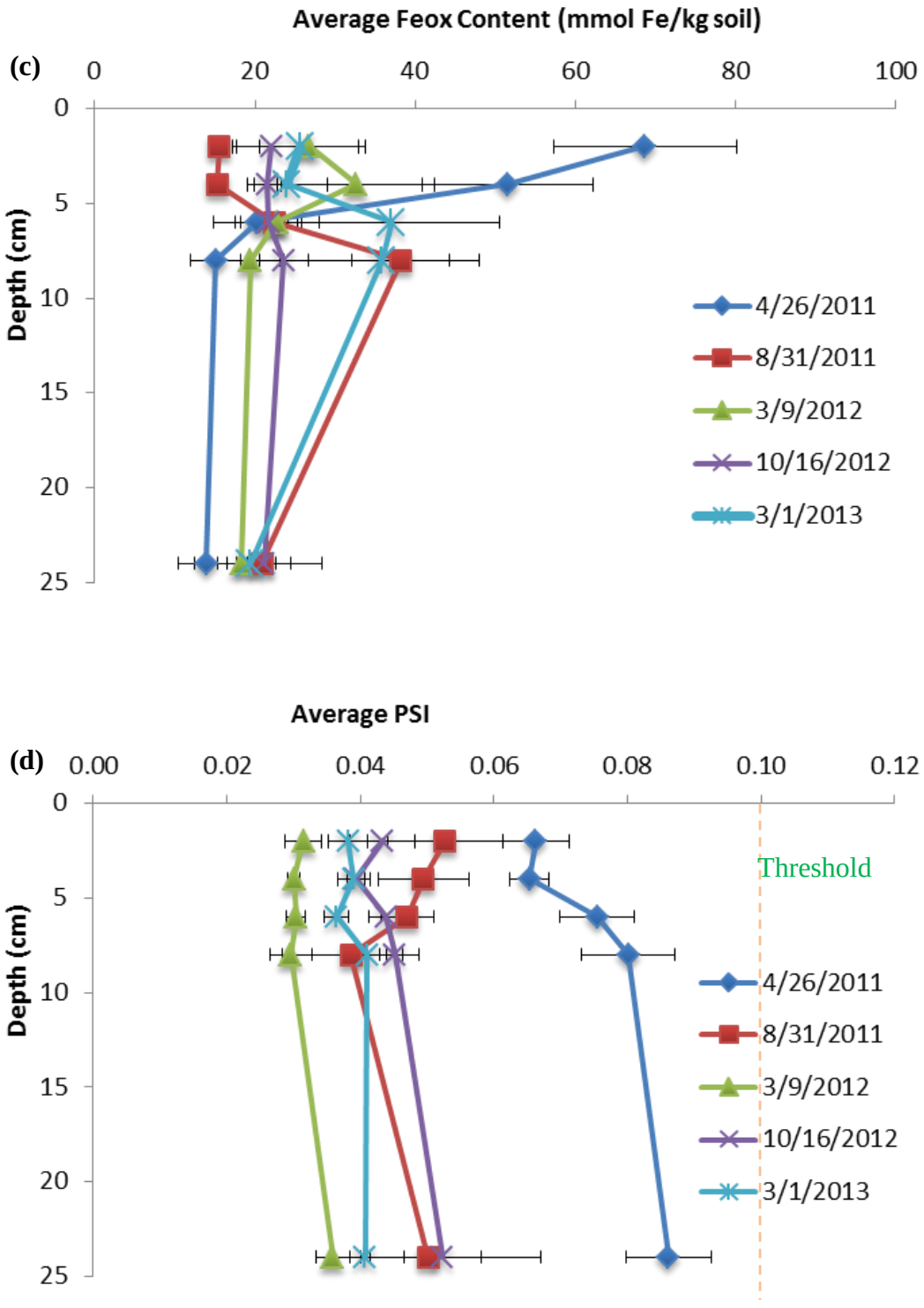
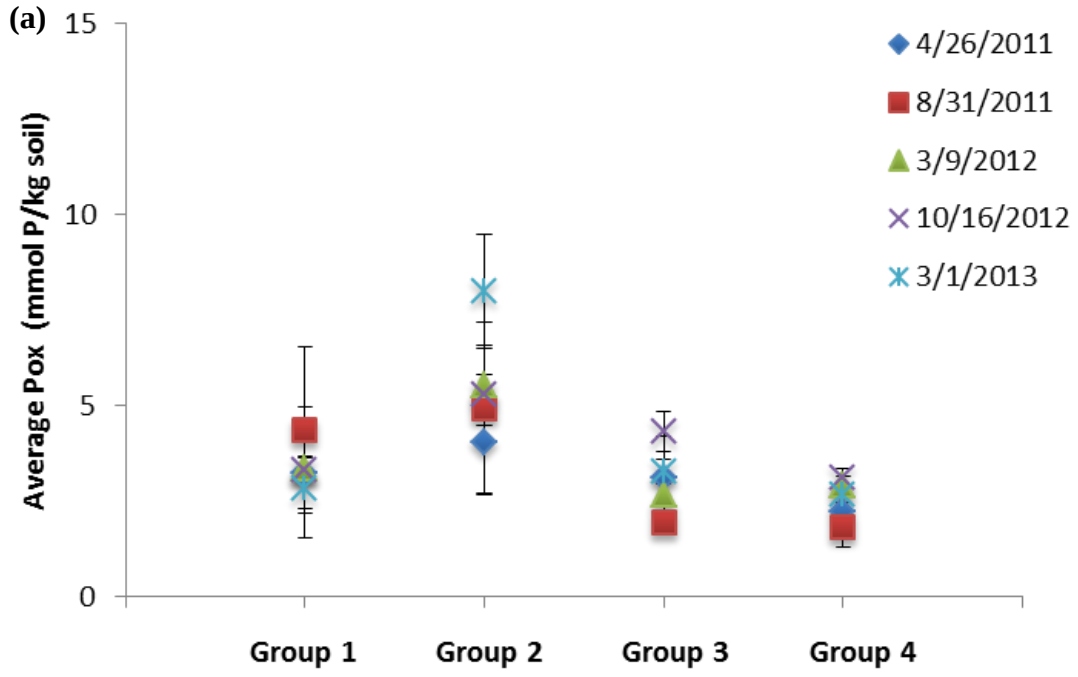
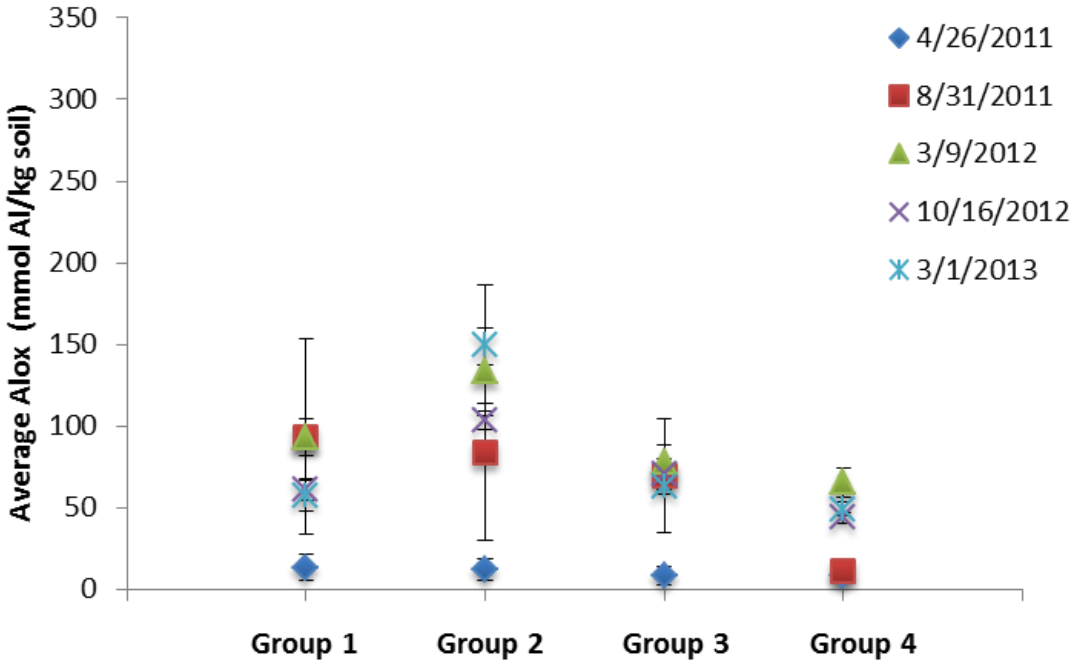


Figure 3-11 Layer average oxalate extractable contents and PSI collected at enhanced P removal bioretention site during the entire experimental running period: (a) P_{ox}; (b) Al_{ox}; (c) Fe_{ox}; (d) PSI.

(a)


Average Pox (mmol P/kg soil)
15
10
5
0
Group 1
Group 2
Group 3
Group 4
4/26/2011
8/31/2011
3/9/2012
10/16/2012
3/1/2013

(b)


Average Alox (mmol Al/kg soil)
350
300
250
200
150
100
50
0
Group 1
Group 2
Group 3
Group 4
4/26/2011
8/31/2011
3/9/2012
10/16/2012
3/1/2013

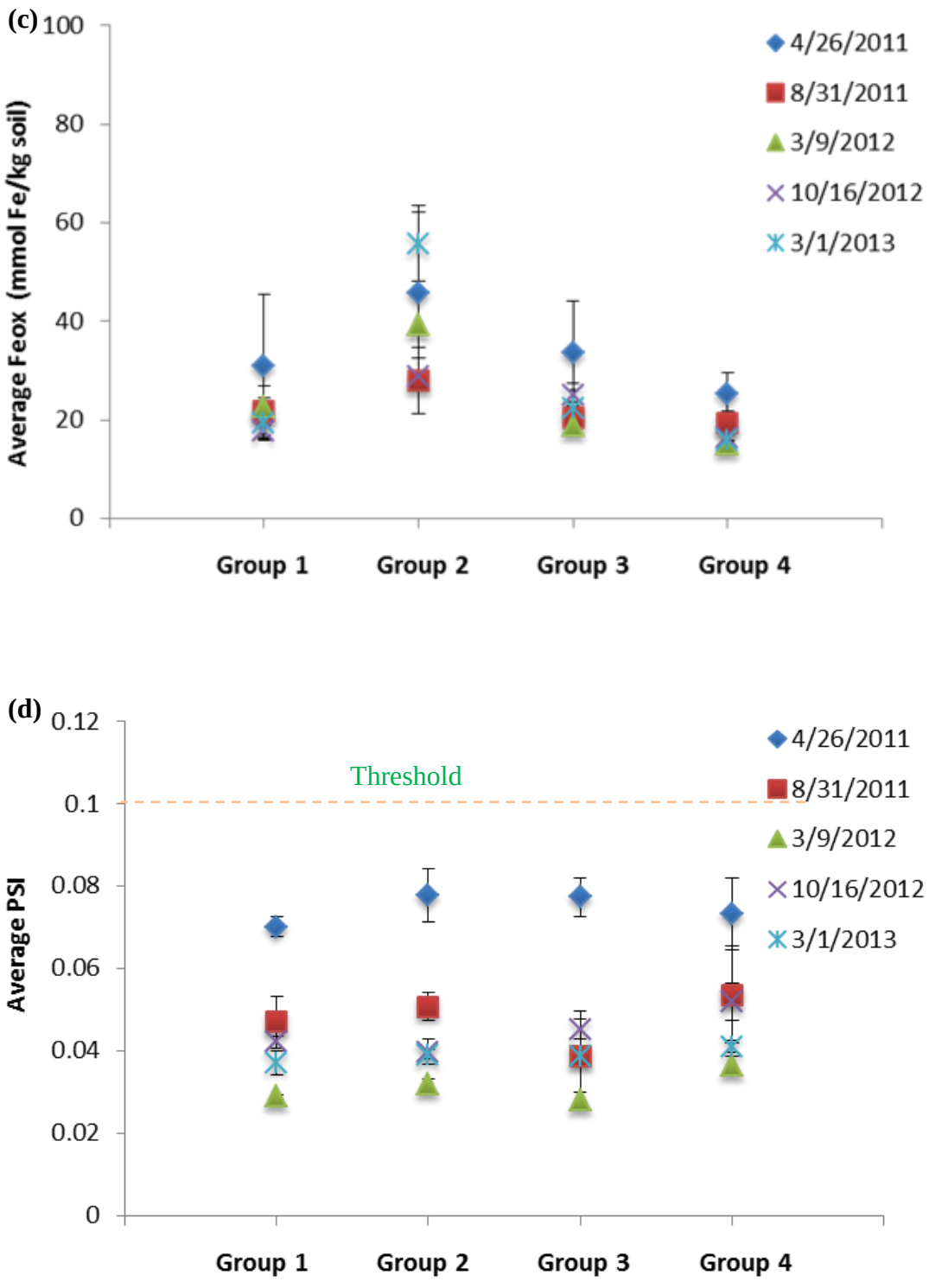


Figure 3-12 Group average oxalate extractable contents and PSI collected at enhanced P removal bioretention site during running period: (a) P_{ox}; (b) Al_{ox}; (c) Fe_{ox}; (d) PSI.

3.3.3 Mass Balance and Mass Accumulation

As mentioned in Section 2.3.1, the WTR retrofit may have modified the media slope; runoff coming into the cell may be unable to migrate far from the inlet, resulting in only a small area of the bioretention site being utilized. Seeing from Figure 2-6, although the field-determined BAV is 6.88 m^3, most of the storms started to have the outflow when the inflow volume higher than 11.5 m^3, which is about 30% of the calculated Ave BAV (38.2 m^3). This indicates that the utilization of the P1 site was only 30% of the total surface area (181 m^2), which is equivalent of 54.3 m^2. As a result, the mass balance calculation was made in a trapezoidal area (length = 12 m, width = 4.2 m to 4.8 m; area = 54 m^2) near the flume inlet with a media depth of 40 cm (Figure 3-13). The segment was divided into 5 layers (2 cm / 2 cm / 4 cm / 4 cm / 28 cm) and 3 groups (4.5 m / 3 m / 4.5 m) for 15 small segments. Total mass was calculated by compositing the mass of all of these 15 small segments.

Around 15,000 kg of WTR (moist) was added at the P1 site, which means that almost 1.32 kg P_{ox}, 347 kg Al_{ox} and 9.79 kg Fe_{ox} were brought in by the WTR retrofit. For the mass balance calculation segment, the additional P_{ox}, Al_{ox} and Fe_{ox} were 0.40 kg, 104 kg and 2.93 kg, respectively. The mass balance calculation segment was divided into five layers and three groups, resulting in 15 small segments. The total mass of the oxalate extractable P, Al and Fe were calculated by sum of the mass of all these fifteen small segments. The mass accumulation calculation of the study segment is shown in Figure 3-14 Moreover, the mass based average concentrations were calculated by dividing d the oxalate extractable mass by the total soil mass of the mass balance calculation segment, which are summarized in Table 3-5.

From Figure 3-14(a), it can be seen that P_{ox} increased after the WTR retrofit (August 31, 2011), but at a much higher level than the amount of the WTR addition. This may be due to P accumulation from the stormwater runoff, DOP export by biological processing and P cycling of vegetation in the soil (Lucas and Greenway 2011; Novozymes 2014). Each year, around 0.84 kg TP (3.00 kg/ha-yr × 0.28 ha × 1 yr = 0.84 kg) was brought in by stormwater influent and only 0.13 kg (0.48 kg/ha-yr × 0.28 ha × 1 yr = 0.13 kg) went out; nearly 0.71 kg of TP was retained by the P1 site (calculated using the parameters in Section 2.3.2). The difference in P_{ox} mass between October 16, 2011 and August 31, 2011 was 0.77 kg, and between March 1, 2013 and March 9, 2012 it was 0.90 kg in somewhat agreeing with the stormwater balance (Liu and Davis 2013). However, media P_{ox} values in the spring were lower than in the fall. This may be attributable to plant growth activity. In the early spring, nutrients and water from the media are obtained by seeds and plants in order to facilitate seed germination, seedling development, and organogenesis or new buds building (Grant et al. 2001; Novozymes 2014). During these processes, the uptake of P is far greater than the release. A large amount of P is transported from the media to the vegetation, where it accumulates. From late summer to early fall plant growth slows down, which means there is less need for P. Moreover, falling leaves and biodegradation might also add some P to the media (Lucas and Greenway 2011).

Al_{ox} increased substantially due to the WTR addition, which is in accordance with the results of one way ANOVA tests described in Section 3.3.2, and then remained at an almost constant value (Figure 3-14(b)). However, the increased amount was only 60% of the estimated level, which may be because the WTR was

not evenly spread throughout the entire site, or because some of the Al oxide become crystalline over time and was not oxalate extractable (Katz and Hayes 1995). The WTR amendment also resulted in some Fe_{ox} increase. After the initial increase, the level of Fe_{ox} did not change substantially (Figure 3-14(c)).

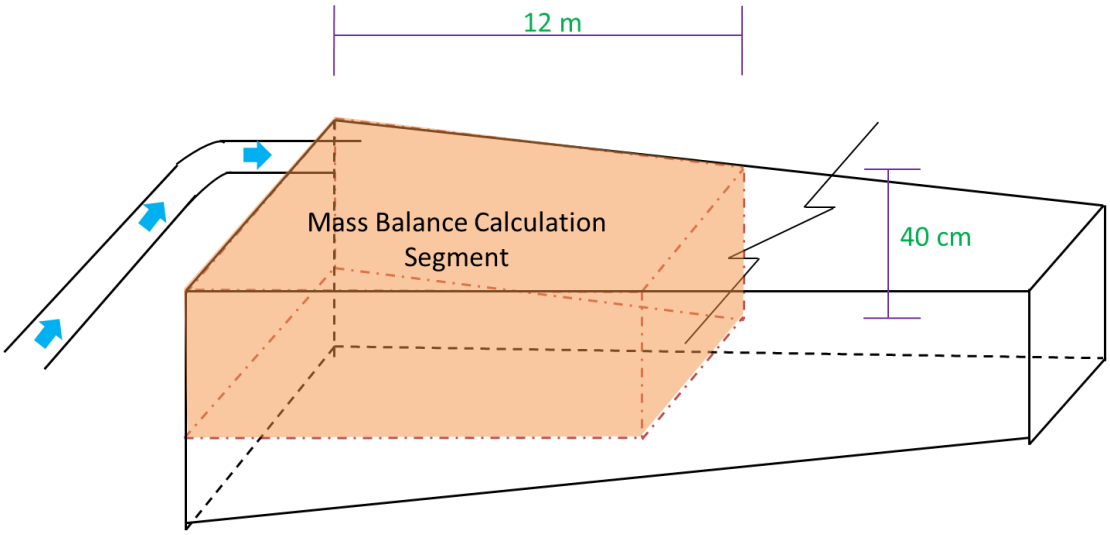
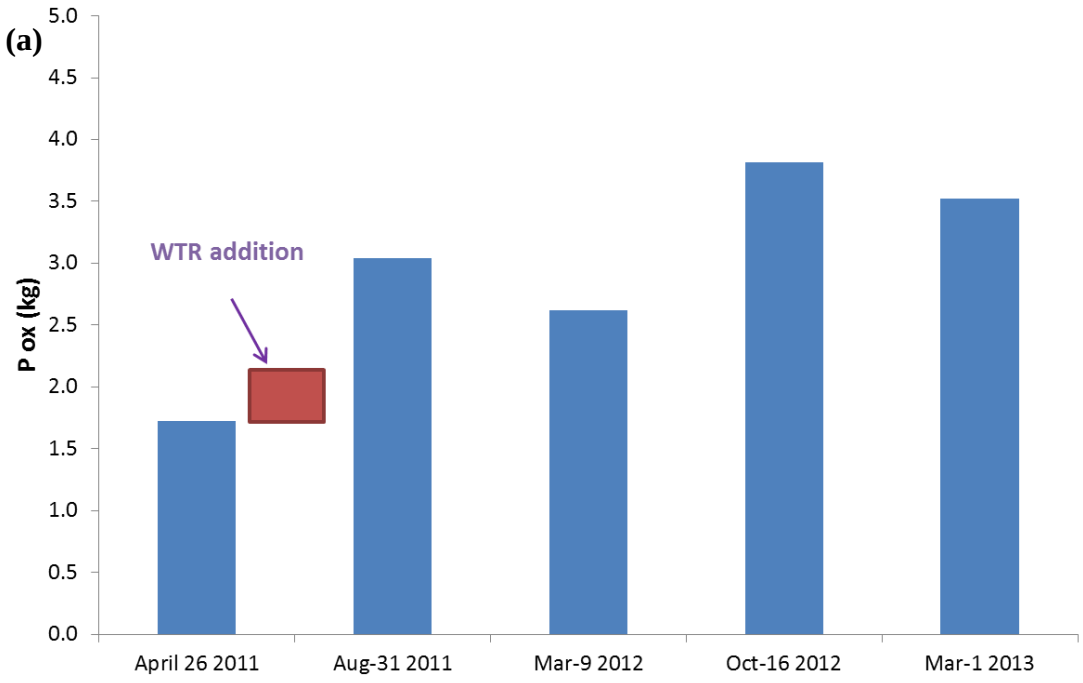
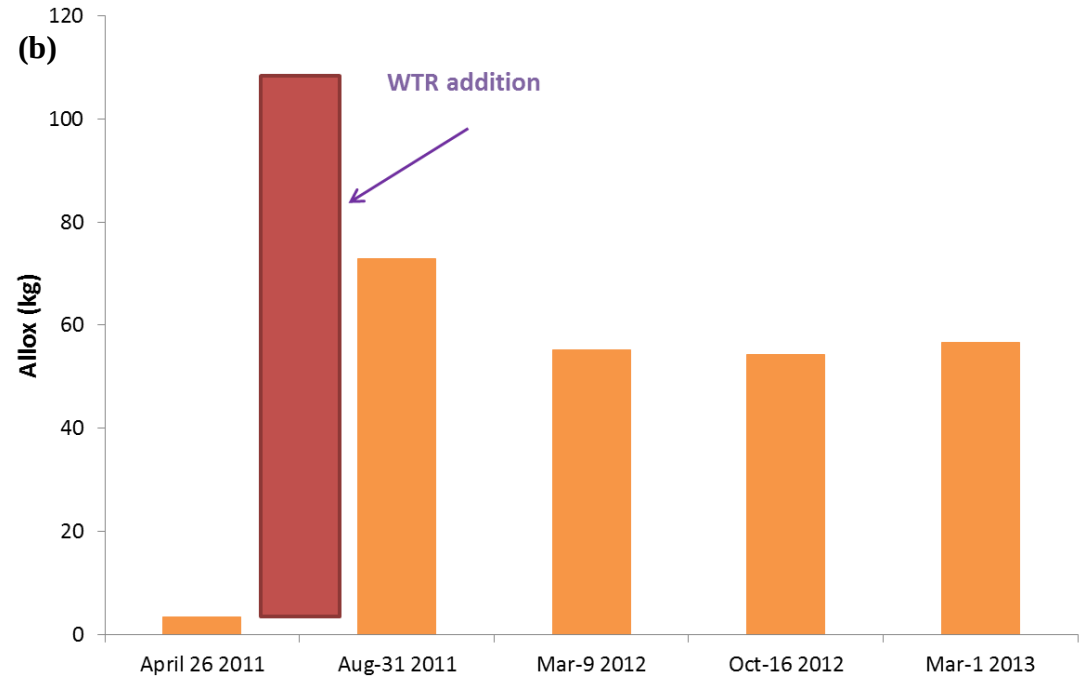


Figure 3-13 Sketch of mass balance calculation for oxalate extractable contents at the enhanced P removal site.

Table 3-5 Mass based average concentrations of oxalate extractable contents.

	P_{ox}	Al_{ox}	Fe_{ox}
	mmol/kg soil		
April 26 2011	1.81	3.98	19.52
Aug-31 2011	3.29	85.04	22.19
Mar-9 2012	2.81	67.21	21.86
Oct-16 2012	4.18	68.49	23.44
Mar-1 2013	4.10	75.36	27.13


(a)
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
P ox (kg)
WTR addition
April 26 2011
Aug-31 2011
Mar-9 2012
Oct-16 2012
Mar-1 2013


(b)
120
100
80
60
40
20
0
Allox (kg)
WTR addition
April 26 2011
Aug-31 2011
Mar-9 2012
Oct-16 2012
Mar-1 2013

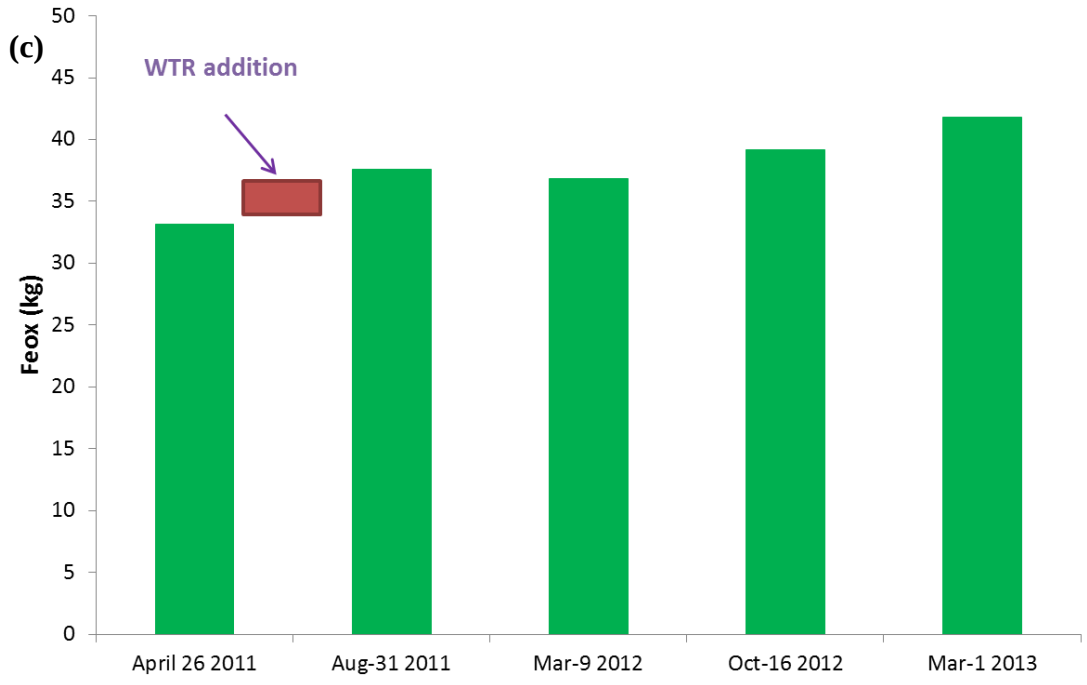


Figure 3-14 Mass accumulation of oxalate extractable P, Al and Fe in the mass balance zone at the enhanced P removal bioretention site: (a) P_{ox}; (b) Al_{ox}; (c) Fe_{ox}.

3.3.4 Leaching of DP from Capture PP.

The P1 site was found to export TP before the retrofit (Li and Davis 2009); however, as can be seen in Figure 3-3(a), since PSI was < 0.1, the risk of P leaching into the P1 site before the retrofit is low. It is hypothesized that this P leaching came from PP captured by the media (Scarlatos 1997; Chen and Sheng 2005; Berretta and Sansalone 2012). In order to test this assumption, an experiment examining Phosphorus leaching from PP was performed and the results are shown in Figure 3-15.

The original stormwater influent had a TP of 1.13 mg/L, with dissolved fraction ($f_d = \frac{DP}{TP}$) of 9.7% (DP = 0.11 mg/L), most of which was DOP (0.10 mg/L). After three days of drying the PP collected from the field runoff, DP (0.11 mg/L f_d =

11.2%) was found to leach when water was added. The dissolved organic fraction ($f_{d-org} = \frac{DOP}{DP}$) was 69.5%. DP leaching was found each time when water was added after each three day drying time. The DP value decreased to 0.06 mg/L on the second round (Day 7), which is about half that of the first leaching concentration. It then decreased to 0.03 mg/L on the third round (Day 10), which is about a quarter of the first leaching concentration. Finally, it stayed at that level (0.04 mg/L) through the fourth round (Day 13). The $f_{d\text{-}org}$ for each round was similar (70% - 75%), corroborating the hypothesis that DP leaching resulted from the particulate matter in the P1 site. This observation agrees with the observations made by other researchers (Scarlatos 1997; Chen and Sheng 2005; Berretta and Sansalone 2012), that PP that was filtered and accumulated from urban stormwater could potentially partition back to the aqueous phase. Moreover, DOP is the major component.

Adsorption and/or precipitation have been recognized as the two primary mechanisms for SRP well retention in bioretention systems (Erickson et al. 2007; Hsieh et al. 2007a; Wu and Sansalone 2013). In the water quality research described in Chapter 2 (see Table 2-2), the output EMCs (based on the cumulative mass divided by the cumulative volume for all collected samples) of SRP and DOP were identified as 0.037 mg/L and 0.028 mg/L, respectively. DOP accounts for 43% of DP, compared to the results of this leaching study which found that $f_{d\text{-}org}$ = 67%, indicating that DOP was managed well by WTR addition, as well as SRP. Karathanasis and Shumaker (2009) found that with hydroxide minerals present in soil media, organic phosphorus can be sorbed in greater quantities and with a higher energy than inorganic phosphorus.

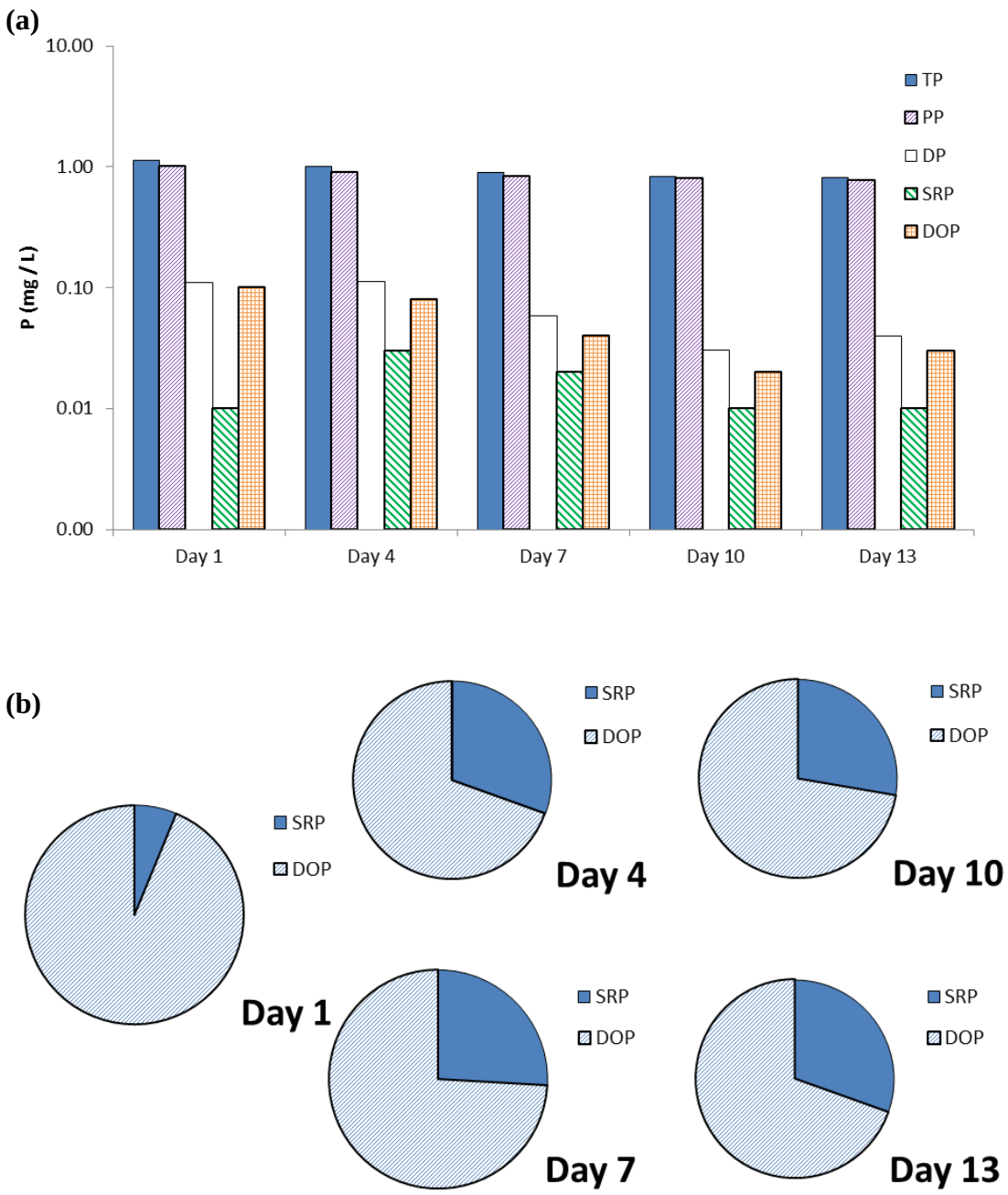


Figure 3-15 DP leaching from captured PP test: (a) P species; (b) fractions of dissolved P.

3.4 Summary

This field media performance study follows the hydrology and water quality study for enhanced P removal bioretention system.

The incorporation of WTR significantly increased the amount of amorphous aluminum and iron (Al_{ox} + Fe_{ox}) of the P1 site, resulting in a PSI decrease (from around 0.075 to 0.031 – 0.048), which implies that the P sorption capacity was enhanced by the WTR addition (Kleinman et al. 2000; Agyin-Birikorang and O'Connor 2007).

P distribution had a strong correlation with the runoff path. It is much easier for P to accumulate in the top media and it occurs in higher amounts closer to the runoff inlet. Before retrofit, since most of the amorphous Al and Fe were brought by the runoff and accrued in the surface media, the P sorption capacity decreased with deeper media. However, the P adsorption depth in the media was enlarged after the retrofit. Additionally, the PSI values did not change significantly and always remained below 0.05 after the retrofit, indicating that the WTR amendment continued to work well after two years of operation.

The mass balance calculation, compared to the water quality analysis, demonstrated that the media P continued to increase during the running period, mostly due to the accumulation from stormwater runoff. However, the media P values in the spring were lower than in the fall, which may be due to plant growth activity. Both SRP and DOP leaching resulted from captured PP during a laboratory leaching study; DOP leached almost twice as much as SRP. Since SRP was slightly higher than DOP in the output of the P1 site (as described in Chapter 2), it can be extrapolated that both DOP and SRP were well managed by the WTR addition.

WTR can strengthen the sorption capacity for both SRP and DOP, achieving enhanced P removal for urban stormwater. This appears to be a feasible method for retrofitting traditional stormwater control measures of enhanced P removal.

Chapter 4: Porous Pavement/Denitrification Vault Treatment Train for Enhanced Nitrogen Removal

4.1 Introduction

Nitrogen (N) is essential nutrient for plant growth; excessive input to water bodies will result in N saturation, eutrophication and algal blooms in surface water, leading to poor water quality and loss of biodiversity in the aquatic ecosystem, even causing adverse health effects on human by contamination of drinking water (Stumm and Morgan 1996; Collins et al. 2010; Ergas et al. 2010). Consequently, more and more attention has been paid to N regulation in urban stormwater.

Various sources of nitrogen compounds in stormwater runoff include fertilizers, animal wastes, plant decay and atmospheric deposition (Davis et al. 2006; Collins et al. 2010), and the typical TN concentrations (event mean concentration (EMC)) in urban storm events are approximately 1 to 3 mg/L for land use (Collins et al. 2010). Nitrogen in water can be present in a variety of forms depending on the water's pH and redox characteristics, including ammonium-nitrogen (NH_4^+), nitrate-nitrogen (NO_3^-), nitrite-nitrogen (NO_2^-), dissolved organic N (DON), and particulate organic N (PON) (Li and Davis 2014).

N can either be transformed from one species to another, or be removed temporarily by assimilation and adsorption processes (Collins et al. 2010). NH_4^+ is a common reduced form of N and can be microbially transformed to NO_2^- and NO_3^- in

the presence of oxygen during nitrification process. Organic N can undergo ammonification to NH_4^+, and nitrification to NO_3^-. Nitrogen assimilation is the process by which inorganic N (NH_4^+, NO_3^-, NO_2^-) is transformed into microbial or plant biomass and temporarily stored as organic N. NH_4^+ can also be removed through adsorption onto negatively charged soil particles. Denitrification results in the permanent removal of N (Collins et al. 2010). During which process, nitrogen oxides (NO_x) is conversed to nitrogen gas (N_2) under an anoxic environment with organic carbon provided.

Moderate-to-poor ammonium and nitrate removal, with nitrate export observed in some instances, has been reported in bioretention system studies (Hatt et al. 2009; Li and Davis 2009; Li and Davis 2014). The likely reason is that the nitrification process occurs in the bioretention cell between storm events (Davis et al. 2001; Hsieh and Davis 2005; Cho et al. 2009). Since nitrate is an anion, it cannot attach to soil and soil particles. It is very mobile and can easily be washed from the soil and transported into receiving waters (Davis and McCuen 2005).

As a result, the promotion of denitrification is one suggested way of enhancing N removal. Some studies have reported that bioretention systems with an internal saturated zone can promote denitrification by creating anoxic conditions (Kim et al. 2003; Dietz and Clausen 2005b; Davis 2007; Hsieh et al. 2007b; Ergas et al. 2010). Pilot-scale experiments were conducted with bioretention systems incorporating aerobic nitrification and anoxic denitrification zones with sulfur or wood chips as denitrification substrates, during which more than 88% of TN removal

efficiencies were found in both units (Ergas et al. 2010). Hunt's field-scale research performed in North Carolina showed a high capacity for nitrate removal (75%) with anoxic storage zones (Hunt et al. 2006). However, concentrations of TKN, NH_4^+ and TN in effluent were higher than in influent, a condition attributable to the conversion of organic forms of nitrogen to NH_4^+. Two bioretention cells were monitored at a study conducted on the University of Maryland campus; one cell contained an anoxic layer. Although no significant differences in the nitrate reductions by the two cells were reported, high mass removals of nitrate at 90% and 95% were observed. The results were attributed to a denitrification processes occurring in the saturated zones of both cells (Davis 2007).

Carbon sources, electron donors, contact time, composition of bioretention media, and vegetation are all important factors affecting the denitrification process. Kim et al. (2003) reported that using woodchips, alfalfa, and newspaper as carbon sources promoted 100% nitrate removal in a laboratory column study. Robertson (2010) found that woodchips can work as long as 10 years as an effective carbon source for denitrification in agricultural runoff. In Smith's research, a longer contact time promoted denitrification (Smith 2008). Finer-textured soils support more denitrification due to their higher capacity for retaining water in soil microsites (Hunt et al. 2006; Hsieh et al. 2007b; Cho et al. 2009). Wood-based media, which are inexpensive, readily available, have considerable longevity and require a low level of maintenance are excellent electron donors for denitrification vaults (Robertson et al. 2005; Robertson 2010).

Pervious pavement is another recommended type of green infrastructure, which has been proven to be extremely effective in infiltrating stormwater runoff (Dietz 2007). Gilbert and Clausen (2006) conducted research in Connecticut which concluded that, as compared to asphalt driveways, the levels of nitrogen species (NO_3^- , NH_4^+ , TKN) in the runoff from UNI Ecostone® driveways were significantly lower. A comparison of performance in controlling stormwater runoff was taken between porous pavements parking lot and asphalt parking lot by Dreelin et al. (2006). Porous pavements were found to have the advantage in treating metals and TP, but the same effect was not found for TN. Collins et al. (2009) evaluated nitrogen species removal for four different type of permeable pavement and standard asphalt in eastern North Carolina, finding although no significant different of TN concentrations between porous pavement and standard asphalt, the NH_4^+ and TKN concentrations were lower and NO_x concentrations were higher in all the permeable pavements except one.

Although numerous studies have been undertaken on the nitrogen-enhanced removal process for urban stormwater, single stormwater control measurements still lack the ability to effectively mitigate nitrogen concentrations. A combination of two or more technologies together is a promising possibility for even greater success in N removal. Robertson et al. (2005) combined a sand filter and a denitrification filter together to treat septic tank effluent in four full-scale sites. Results indicated that denitrification filters significantly reduced NO_3^- amounts from 87% to 98%.

Peterson (2013) recommended that N reduction in stormwater runoff can be improved by installing a stepped system with the combination of a filter and a saturated denitrification layer.

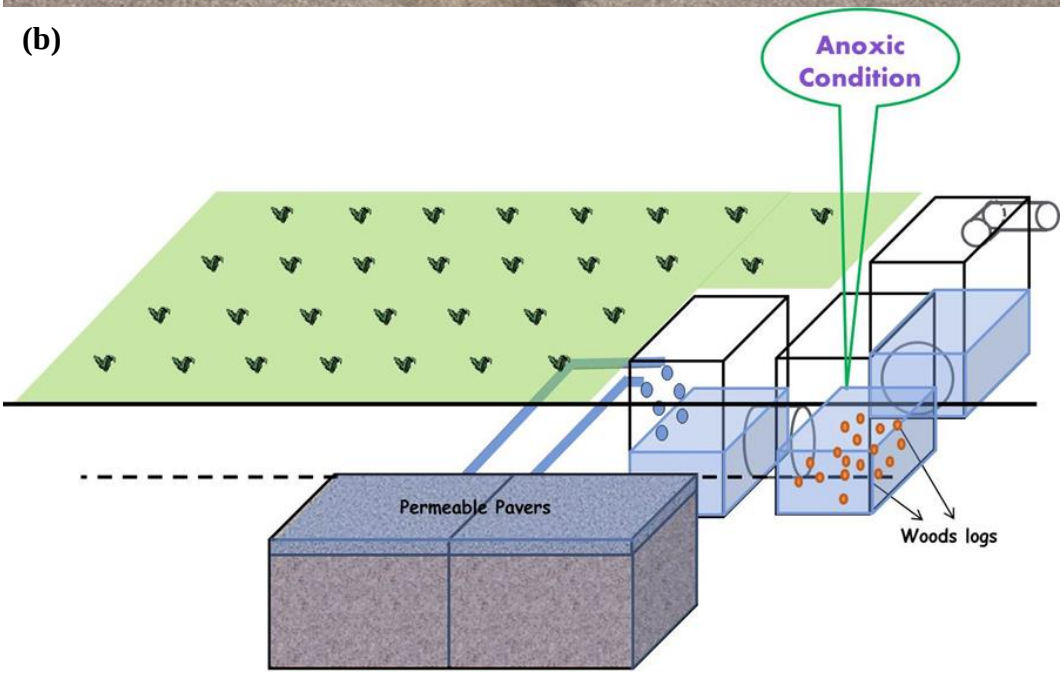
This field study is made by combining porous pavement and denitrification vaults together as a treatment train in an attempt to produce a nitrogen-neutral parking lot. The pavement-infiltrated water drained directly into three submerged vaults with oak logs added to provide a carbon source for denitrification and to maintain anoxic conditions. All N species (TN, DN, NO_2^-, NO_3^-, NH_4^+) were monitored. The goals of this research were to (i) evaluate the water quality produced by the treatment train to see if it achieved good N removal; (ii) assess if the treatment train had advantages in N removal compared with a bioretention system; and (iii) clarify the reaction mechanisms in each stage of the treatment train; (iv) examine the water balance for porous pavements.

4.2 Methodology

4.2.1 Site Description

The 80 m^2 (lined) porous pavement was installed on the campus of the University of Maryland, College Park, to collect stormwater runoff from a small parking lot. The infiltrated water drained directly into three submerged vaults (H = 1.6 m, A = 5.2 m^2), to which around 0.1 m^3 of willow oak logs were added to provide a carbon source for denitrification and to maintain anoxic conditions. Willow oak is a native hardwood. The willow oak used for this experiment was cultivated at the Arboretum and Botanical Garden at the University of Maryland, College Park. The

site construction work was completed in December of 2012. The site was studied from August 2013 to May 2014. Diagrams of the N1 site and the construction work performed there are shown in Figure 4-1 and Figure 4-2, respectively.



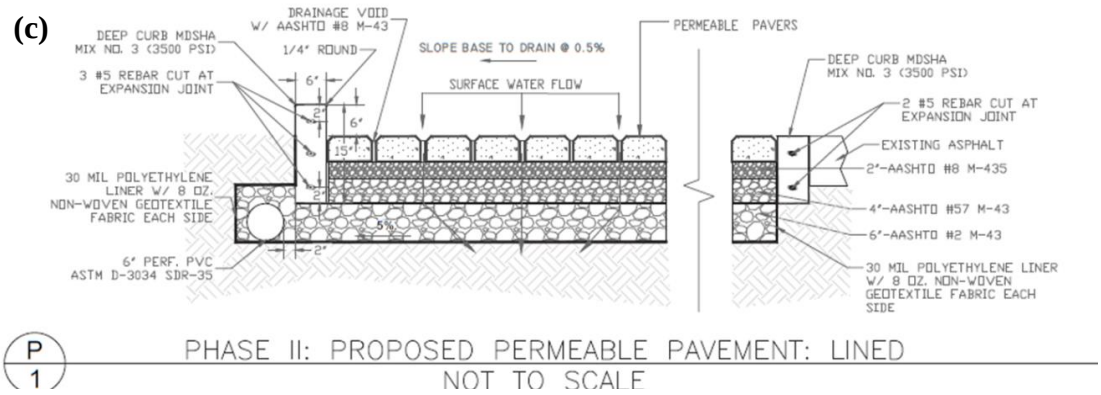


Figure 4-1 Enhanced N removal site diagram: (a) site picture; and (b) 3-D site configuration sketch; (c) design drawing for porous pavement.

Figure 4-2 Enhanced N removal site construction process.

4.2.2 Monitoring and Sampling Methodology

Stormwater runoff drains into the porous pavement, collected by the 15-cm underdrain PVC pipe with a plug-in 15-cm Thel-Mar weir outfitted in the outlet, then goes into the submerged denitrification vaults. There were two monitoring points in the system, one for under-drained water from porous pavement (NM1) and the other for water in the denitrification vaults (NM2). ISCO Avalanche autosamplers equipped with bubble flow meters (730 Bubbler) were assigned to both monitoring points. A recording rain gauge (674 Rain Gauge) with a 0.0254 cm level of sensitivity was connected to one of the autosamplers on the site to record the rainfall depth. A water level logger (WL16 Water Level Data Logger, Global Water, 0-15 ft) and a data-logging water quality sensor (AquiStar TempHion ^{TM} Submersible Smart pH/ORP Sensor with Data Logging, Geotech) were placed in the bottom of the denitrification vaults to record the water level and on-site water quality parameters (temperature, pH, ORP), respectively. The monitoring devices are shown in Figure 4-3.

During a storm event, the sampling program was set to collect fourteen samples (400 mL sample in 950-mL poly bottles) with different sample times for both NM1 and NM2. 400 mL samples were collected every one or two days from NM2 during the dry period by manually operating the ISCO Avalanche autosampler. A rigorous QA/QC was implemented throughout all of the processes of sample collection, storage, and analysis; this implementation was described in Section 2.2.2.

Wood logs

Thel-mar weir

ISCO Avalanche auto-samplers

Figure 4-3 Monitoring devices at the enhanced N removal site.

4.2.3 Analytical Procedures

The water quality parameters analyzed in the laboratory included: TN, dissolved nitrogen (DN), nitrate (NO_3^-), nitrite (NO_2^-) and ammonium nitrogen (NH_4^+). Particulate organic nitrogen (PON = TN - DN), dissolved organic nitrogen (DON = DN – NO_3^- – NO_2^- – NH_4^+), total organic nitrogen (TON = PON + DON), and nitrogen oxides (NO_x = NO_2^- + NO_3^-) were all calculated from direct N measurements.

DN, NO_2^- , NO_3^- and NH_4^+ samples were first filtered through a 0.22 μm membrane filter. TN and DN were then prepared using persulfate digestion (4500-N C) and colorimetric determination by the ultraviolet spectrophotometric screening

method (4500-NO_3^- B) scan from 220 - 275 nm (Agilent Technologies Cary 60 UV-Vis, Kyoto, Japan). NO_2^- and NH_4^+ were tested using the Colorimetric Method (4500-NO_2^- B) and Phenate Method (4500-NH_3 F) at 543 nm and 640 nm (Agilent Technologies Cary 60 UV-Vis, Kyoto, Japan), respectively. NO_3^- was analyzed using the Ion Chromatographic Method (4110-NO_3^-) by an ion chromatography system (DIONEX ICS-1100, Sunnyvale, CA) with an automated sampler (DIONEX AS40, Sunnyvale, CA).

Nitrogen species are reported both in concentration (N mg/L) and composition (% of TN). Half of the detection limit value was used for statistical analysis if the measured value was more than 15% lower than the detection limit. The detection limit was 0.10 N mg N/L for TN, DN and NO_3^-, 0.05 mg N/L for NH_4^+ and 0.01 mg N/L for NO_2^-.

4.2.4 Data Handling and Statistical Analyses

Since the original ORP values monitored in this study was referred to an Ag/AgCl electrode, "230 mV" was added to the raw data (convert to the Hydrogen reference electrode readings).

As described in Section 2.2.4, runoff volumes, *V*, were calculated using Equation 2-1; overall cumulative input/output pollutant masses, *M*, were calculated using Equation 2-2; the Event Mean Concentration (EMC) is calculated using Equation 2-3; the annual pollutant mass loads produced or discharged per unit drainage area (L, kg/ha-yr) were calculated using Equation 2-4.

Pollutant duration curves were created to focus on the performance of instantaneous pollutant concentrations in the denitrification vaults. An assumption was made that the daily grab samples accounted for six hours of duration. The exceedance probability plots and a Wilcoxon rank-sum test were employed to evaluate the differences in N concentrations between porous pavement effluent and the contents of the denitrification vaults.

4.3 Results and Discussion

This site was monitored continuously for ten months, from August 2013 through May 2014. During this period, 52 storm events were monitored. Rainfall depth and vault depth data were monitored during the entire period; onsite pH and redox data were recorded beginning in the middle of December 2013 and continuously thereafter for five subsequent months. Water quality data were collected from September 2013 to April 2014, and included 165 grab samples from the denitrification vaults and time-scheduled porous pavement effluent samples from 21 storm events.

4.3.1 General Trend of a Storm Event

The rainfall depth for the 21 collected events ranged from 0.08 to 10.21 cm. The hydrology performance, and pH and redox conditions of the vault water from April 25, 2014 to May 5, 2014, with a storm on April 29, 2014 (10.21 cm), are presented in Figure 4-4.

These data are characteristic of the entire monitoring period and representative of condition changes during a storm. When it rained, the water depth in the vaults

increased; during dry weather, water was lost at a relatively constant rate, apparently due to leakage from the vault. Based on the design, there should not have been any outflow if the water depth was < 1.6 m. However, outflow was recorded when the water depth was higher than 1.2 m, which only happened 5 times during the entire monitoring period at October 10, 2013, December 29, 2013, January 10, 2014, March 29, 2014 and April 29, 2014. It may have been due to the water-stop wall being unable to stop the water. Water was able to go through the wall and be discharged by the outflow pipe (Figure 4-5). Nonetheless, most of the flow could effectively be managed by the treatment train system due to the dry weather infiltration.

The vault water became aerobic when the flow entered from the pavement (the redox level (ORP) increased from around -340 mV to 100 mV, whereas pH decreased from around 8.0 to 7.2). This aerobic condition in the vaults was maintained for a short amount of time (from a couple of hours up to a dozens of hours), depending upon the duration of the rainfall. After that, the vaults provided sufficient detention time and anoxic conditions (ORP was around -340 mV, pH was around 8.0) to promote denitrification (Blowes et al. 1994). The trend of the pH was in accordance with that of the ORP. Effluent from porous pavement mixed with the vault water. The incoming water should contain oxygen and mixing should add oxygen, which in turn can enhance the nitrification process. The nitrification process created hydrogen ions (H^+) (Equation 1-1, Equation 1-2), which resulted in a pH decrease. The pH increased again to around 8 and was maintained through the dry

period, at which time the pH and denitrifying bacteria were able to reach their highest rates of nitrate reduction (Glass and Silverstein 1998).

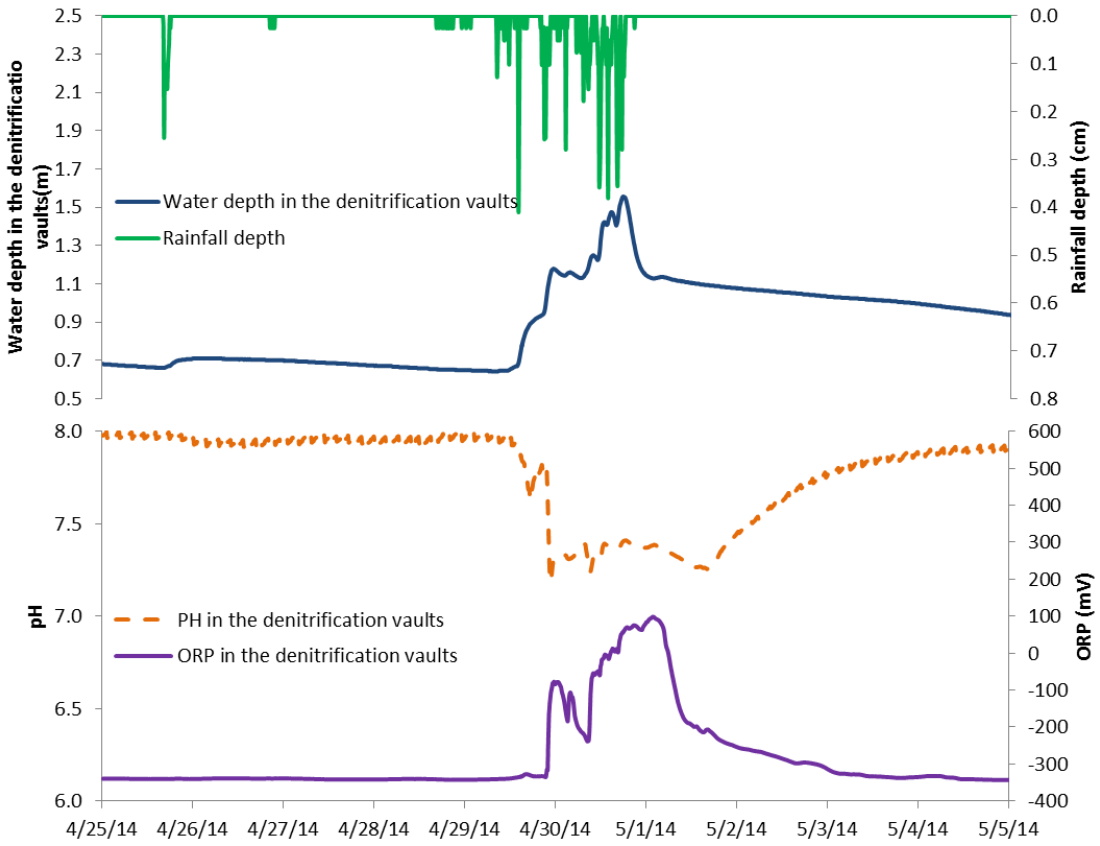


Figure 4-4 Hydrology performance, and pH and redox conditions of the vault water at the enhanced N removal site (April 25 – May 5, 2015).

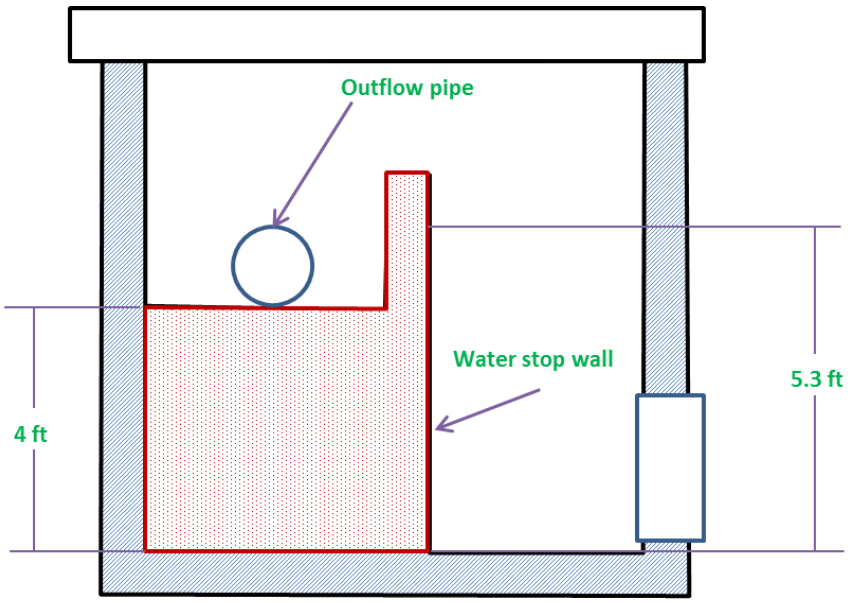


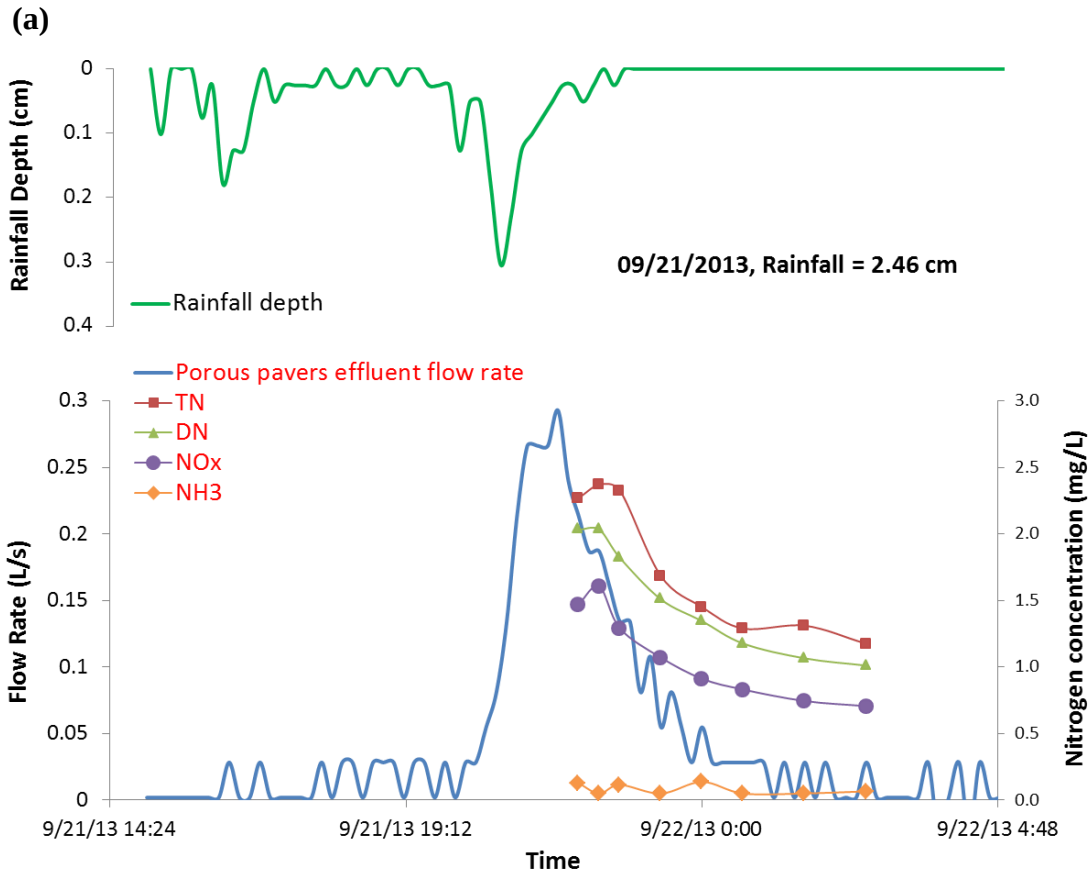
Figure 4-5 Diagram of the 3rd denitrification vault at the enhanced N removal site.

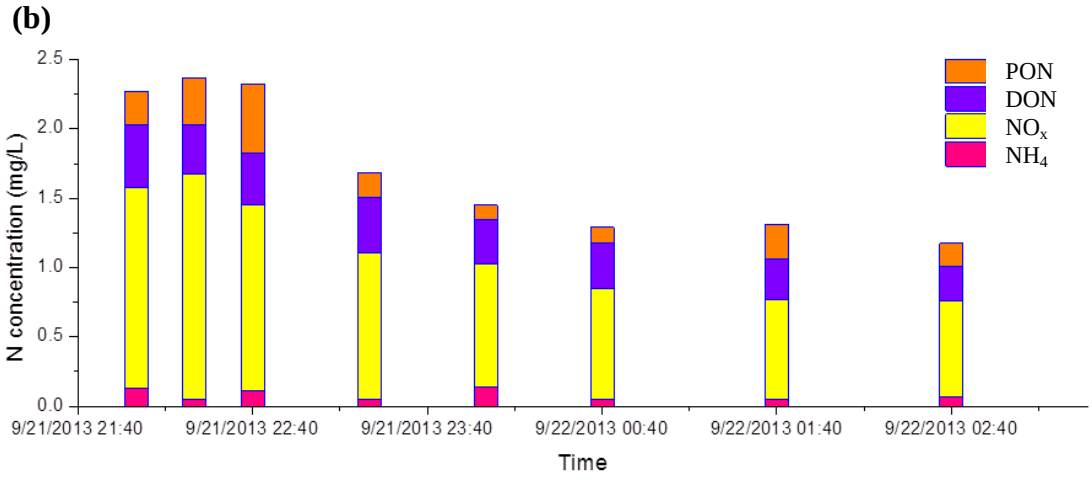
Figure 4-6 shows the general trend of the storm event collected on September 21, 2013 (rainfall = 2.46 cm). The hydrograph of the porous pavement effluent has a shape following the hyetograph, but with broader peaks and peak delays (Figure 4-6(a)); this is similar to the hydrograph of a bioretention SCM (Li et al. 2009; Li and Davis 2014).

The concentrations of nitrogen species in the porous pavement effluent were dynamic (Figure 4-6(b)). The NO_x concentrations exhibited an initial spike before gradually decreasing. This was most likely due to the ammonification and nitrification processes that occurred in the porous pavement between storm events which converted the accumulated organic and ammonia nitrogen into nitrate. The similar process was observed by many researchers in bioretention systems (Davis et al. 2001; Hsieh and Davis 2005; Cho et al. 2009). Because nitrate is an anion, it is unable to attach to soil particles. Furthermore, its mobility allows it to easily be

washed from the soil and transferred to receiving waters (Davis and McCuen 2005). The changes in PON and NH_4^+ showed a similar pattern; this may have been the result of the first flush, which was when the small particles were washed out. After that, most of the PON and NH_4^+ were retained by sedimentation/filtration in the pavers media. DON had no obvious variation during entire process, indicating DON was not leaching from the porous pavement. In this sense, the porous pavement is superior to the bioretention systems, in which large amount of DON leaching was found by Li and Davis (2014).

Figure 4-6 (c) shows the daily change of nitrogen species concentrations in the denitrification vaults after the storm event. Within the first few hours, the concentration of NH_4^+ decreased to an amount lower than the detection limit. This behavior seems to be congruent with our observations illustrated in Figure 4-4: the nitrification process occurred when water came into the denitrification vaults and was kept there for a short time (from a couple of hours to one or two days depending on the rainfall duration). NO_x decreased rapidly in the first two days after the storm (from 0.48 mg/L to 0.26 mg/L), and then slowed until it reached a low level (around 0.1 mg/L). One possible reason for this result could be the denitrification process occurring in the denitrification vaults. The amounts of TN and DN decreased during the dry periods, mainly as a result of the decrease of NO_x. TON (PON + DON) kept a relatively constant rate during the dry period. Other stormwater events followed this patten but differred in the details.


(a)
Rainfall Depth (cm)
0
0.1
0.2
0.3
0.4
09/21/2013, Rainfall = 2.46 cm
Rainfall depth
Porous pavers effluent flow rate
TN
DN
NOx
NH3
Flow Rate (L/s)
0.3
0.25
0.2
0.15
0.1
0.05
0
Nitrogen concentration (mg/L)
3.0
2.5
2.0
1.5
1.0
0.5
0.0
9/21/13 14:24
9/21/13 19:12
9/22/13 0:00
9/22/13 4:48
Time


(b)
N concentration (mg/L)
2.5
2.0
1.5
1.0
0.5
0.0
PON
DON
NOx
NH4
9/21/2013 21:40
9/21/2013 22:40
9/21/2013 23:40
9/22/2013 00:40
9/22/2013 01:40
9/22/2013 02:40
Time

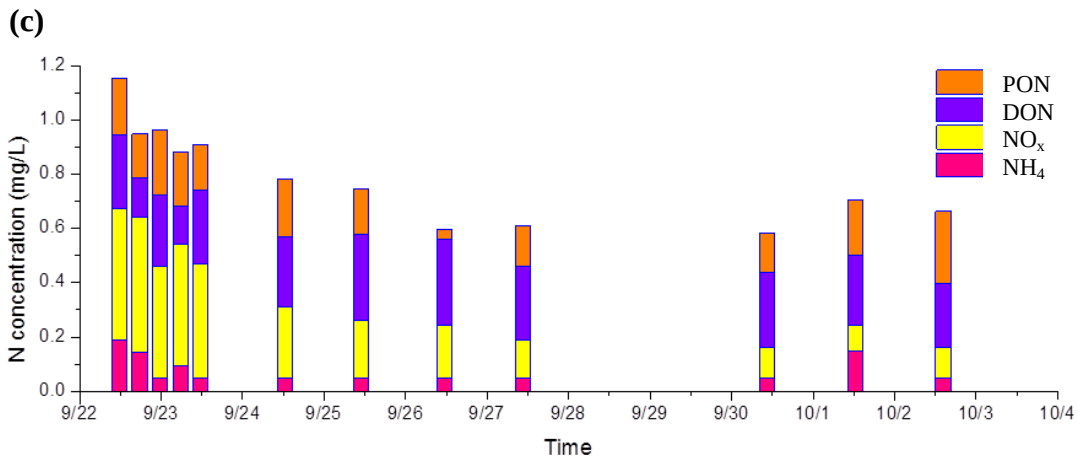


Figure 4-6 General trend of a storm event at the enhanced N removal site (September 21, 2013): (a) porous pavement effluent hydrograph and pollutograph for nitrogen species; (b) distribution of nitrogen species concentrations for porous pavement effluent; and (c) long period distribution of nitrogen species concentrations for water in the denitrification vaults.

4.3.2 N Species Transformations and Removal

Pollutant duration curves and exceedance probability plots for N species are presented in Figure 4-7 and Figure 4-8 in order to characterize the treatment outcome at the N1 site.

TN has a recommended criterion of 0.69 mg/L for rivers and streams (Ecoregion IX) (USEPA 2000). The durations of the TN concentrations of porous pavement and vault water below this criterion were 44% (90 h out of 202 h) and 74% (439 h out of 593 h) for the entire monitored period, respectively (Figure 4-7(a)). In Figure 4-8(a), EMC values for TN in the porous pavement effluent ranged from 0.33 to 2.13 mg/L (median = 0.76 mg/L, 64% exceeded the TN criterion of 0.69 mg/L); in the denitrification vault infiltration water ranged from 0.27 to 0.76 mg/L (median = 0.61 mg/L, 30% exceeded the TN criterion of 0.69 mg/L). TN demonstrated a

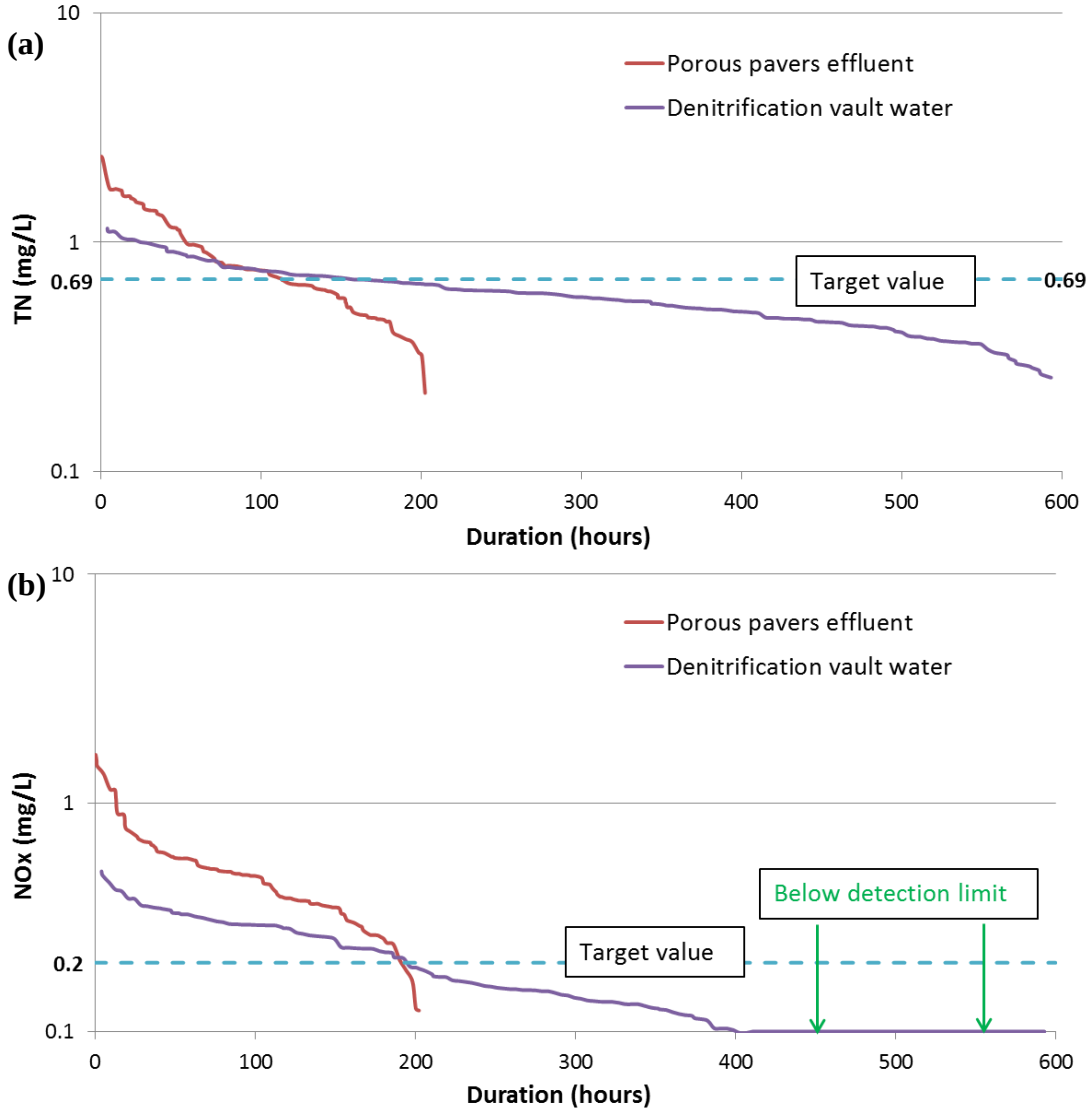
significant reduction (α = 1%) after storage in the denitrification vaults compared to the porous pavement effluent.

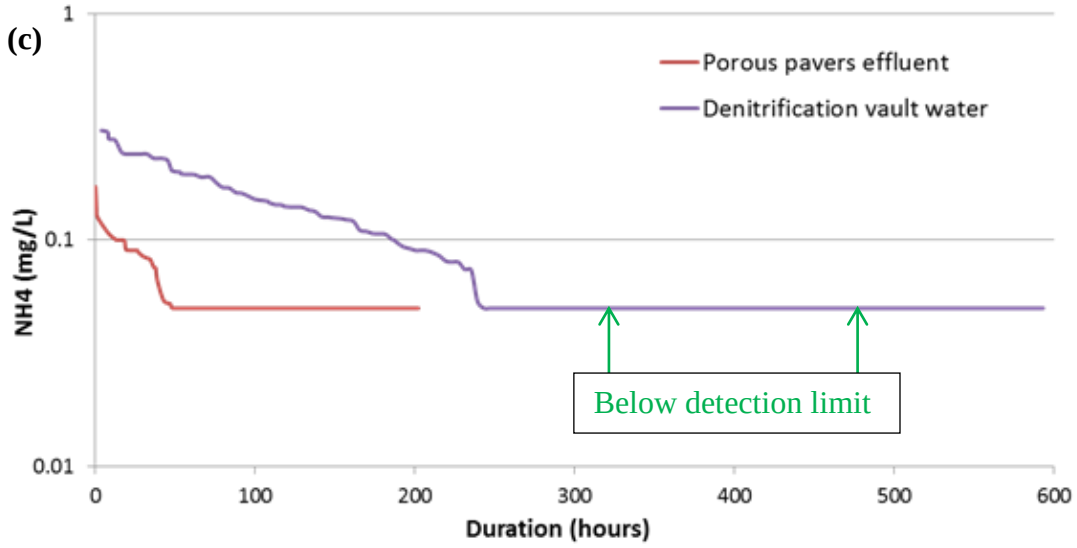
A level of 0.2 mg/L NO_3^- is recommended as a benchmark criterion for excellent water quality in the Potomac River Basin (Davis and McCuen 2005); the porous pavement effluent met this benchmark only 5% (10 h out of 206 h) of the time, whereas the denitrification vault water met it 67% (399 h our of 593 h) of the time (see Figure 4-7(b)). Figure 4-8 (b) shows a large decrease (α = 1%) in NO_x between the porous pavement effluent (0.19 to 1.36 mg/L, median value = 0.48 mg/L) and vault infiltration water (< 0.1 to 0.32 mg/L, median values = 0.15 mg/L), which agrees with the previous statement and indicates that denitrification is occurring in the vaults (Peterson 2013).

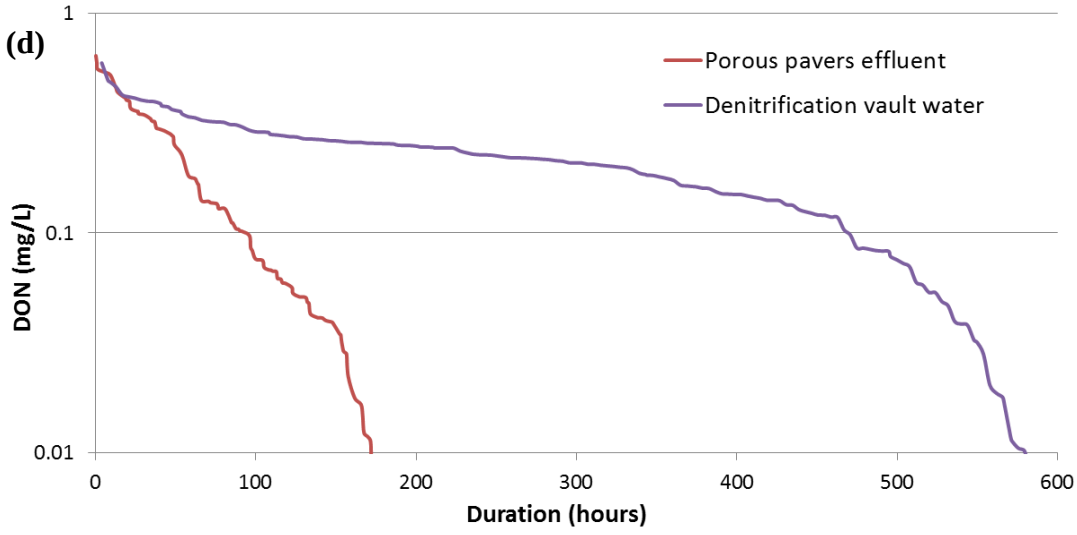
NH_4^+ in the porous pavement effluent and denitrification vaults was below the detection limit (0.05 mg/L) for 76% (157 h out of 206 h) and 58% (343 h out of 593 h) of the time, respectively (Figure 4-7(c)). Although the denitrification vault infiltration water had a wider range (< 0.05 mg/L to 0.22 mg/L) than the porous pavement effluent (< 0.05 mg/L to 0.11 mg/L), no statistically significant (α = 5%) difference was found between the two (Figure 4-8(c)).

The porous pavement effluent EMCs for DON and PON ranged from approximately 0.01 to 0.60 mg/L (median = 0.25 mg/L) and 0.02 to 1.12 mg/L (median = 0.12 mg/L), respectively. Whereas the denitrification vault infiltration water EMCs for DON and PON ranged from 0.01 to 0.37 mg/L (median = 0.20 mg/L) and 0.04 to 0.22 mg/L (median = 0.13 mg/L), respectively. The Wilcoxon rank-sum

test indicated no significant (α = 5%) difference for PON between the porous pavement effluent and denitrification vault infiltration water (Figure 4-8(e)). However, DON was statistically increased (α = 5%) after the water accumulated in the the denitrification vault (Figure 4-8(d)), which may due to the organic matter leaching by the wood logs (Robertson 2010).




(c)
1
0.1
0.01
NH4 (mg/L)
Porous pavers effluent
Denitrification vault water
Below detection limit
0
100
200
300
400
500
600
Duration (hours)


(d)
1
0.1
0.01
DON (mg/L)
Porous pavers effluent
Denitrification vault water
0
100
200
300
400
500
600
Duration (hours)

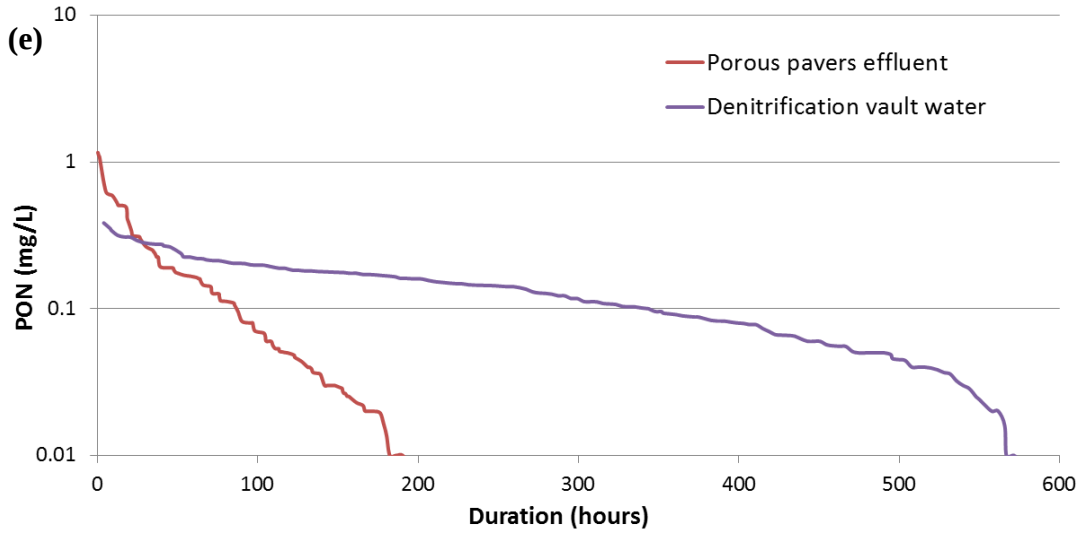
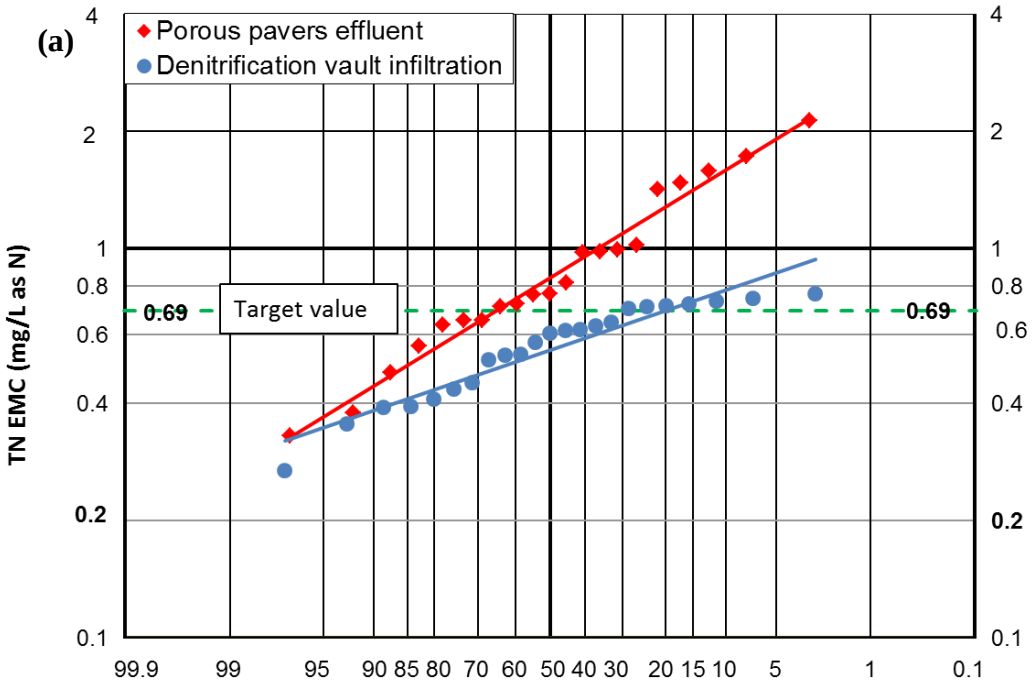
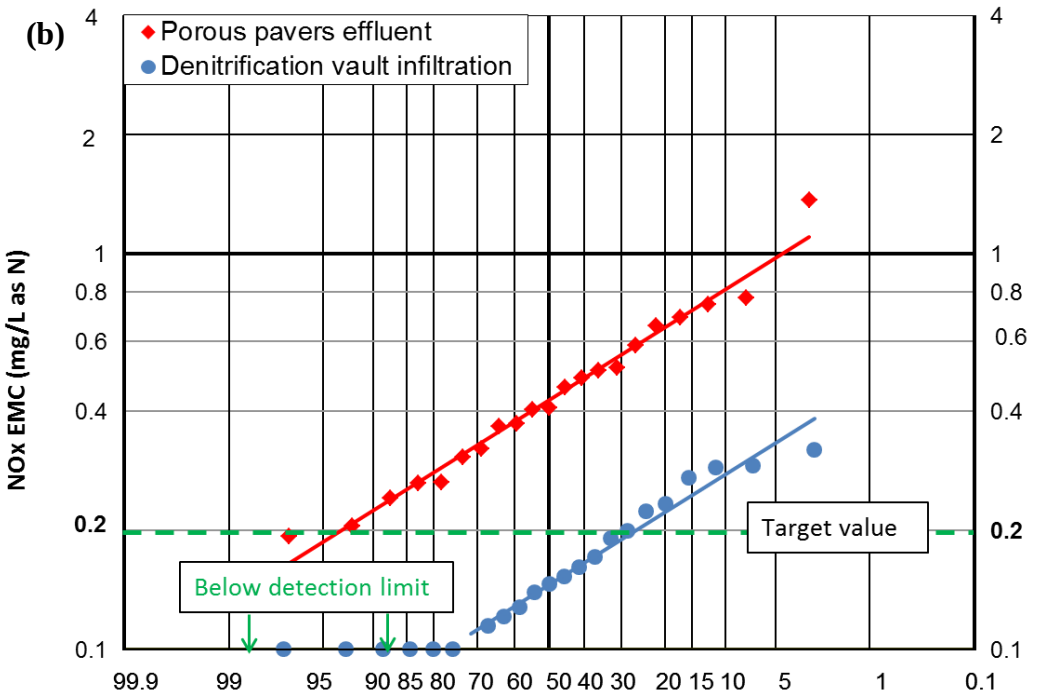
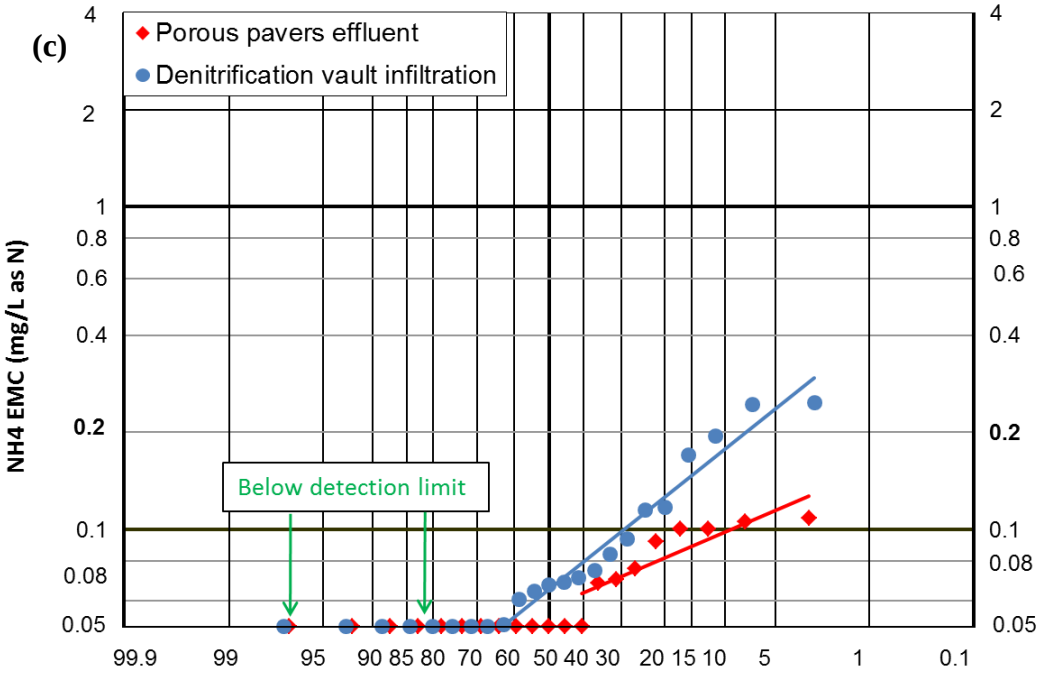


Figure 4-7 Pollutant duration curves for the enhanced N removal site: (a) TN; (b) NO_x; (c) NH_4^+; (d) DON; and (e) PON.




(b)
Porous pavers effluent
Denitrification vault infiltration
NOx EMC (mg/L as N)
4
2
1
0.8
0.6
0.4
0.2
0.1
Target value
Below detection limit
99.9 99 95 90 85 80 70 60 50 40 30 20 15 10 5 1 0.1


(c)
Porous pavers effluent
Denitrification vault infiltration
NH4 EMC (mg/L as N)
4
2
1
0.8
0.6
0.4
0.2
0.1
0.08
0.05
Below detection limit
99.9 99 95 90 85 80 70 60 50 40 30 20 15 10 5 1 0.1

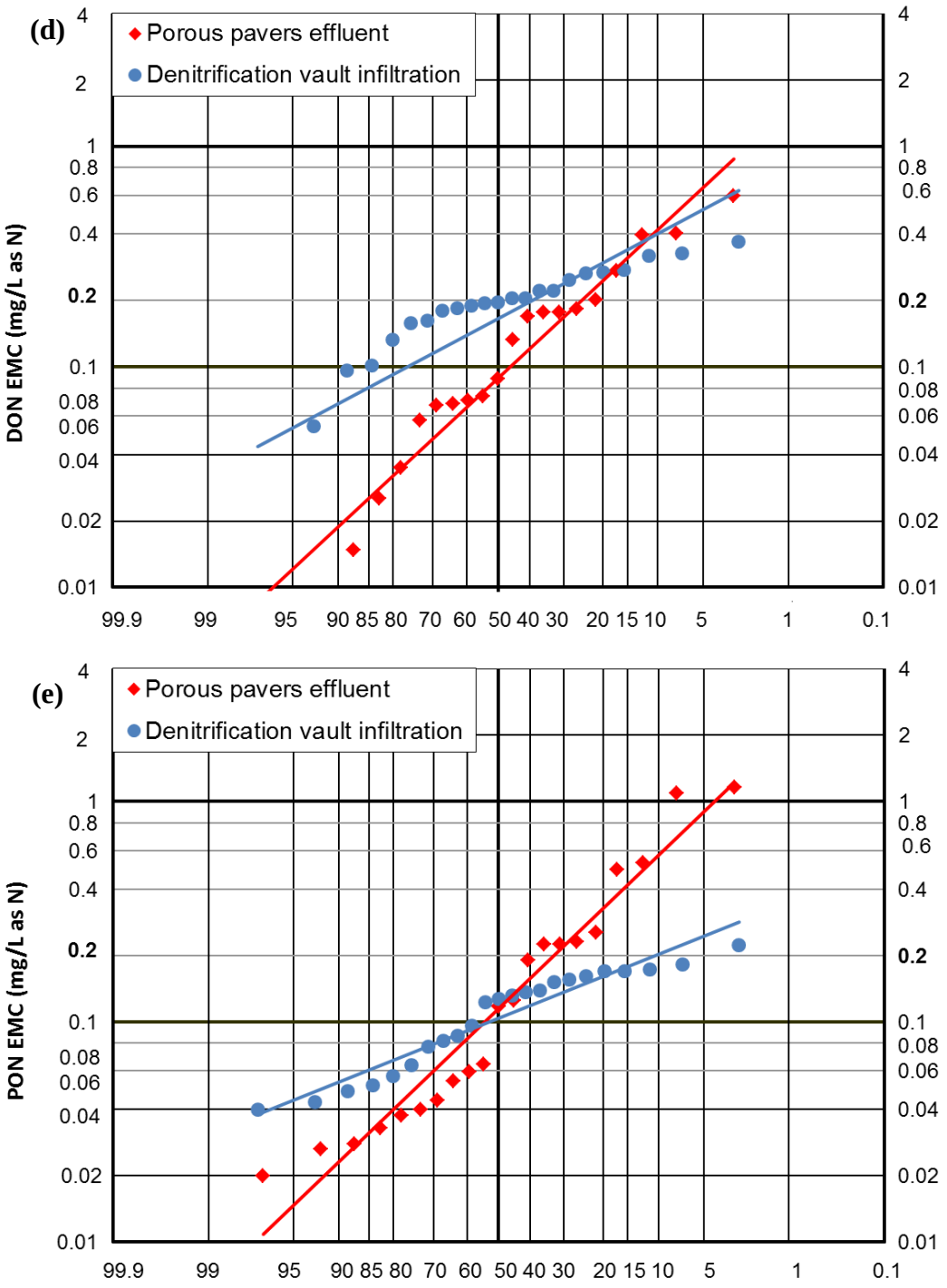


Figure 4-8 Exceedance probability plots for the enhanced N removal site: (a) TN; (b) NO_x; (c) NH_4^+; (d) DON; and (e) PON.

4.3.3 N Behavior and Fate in Porous Pavement/Denitrification Vault Treatment Train

The calculation of annual pollutant loads (L) and pollutant mass reduction (or increase) ratios (R_m) were described in Chapter 2. For the water in the denitrification vault, an assumption was made that the water was continuously leached from the vault at a constant infiltration rate for individual storm events. The infiltration rate was calculated by the depth difference in the vault (usually started with the point just after one storm event to the beginning of next storm event) divided by the corresponding duration. Since stormwater runoff was not collected in this study, the influent and effluent data from the P1 site (described in Chapter 2) were used to for comparison with our current data. Detailed information regarding N removal at the P1 site can be found in the study undertaken by Li and Davis (2014). Detailed information comparing the N1 site to the P1 site can be found in Table 4-1.

Figure 4-9 compares the EMC values (Table 4-1) of all of the nitrogen species for influent and effluent at the P1 site, as well as porous pavement effluent and denitrification vault water at the N1 site.

The porous pavement/denitrification vault treatment train was designed to have two stages. In the first stage, the porous pavement worked as a filter capable of removing most of the particulate matter and providing aerobic conditions to drive nitrification; in this stage, PON was satisfactorily retained by sedimentation/filtration. Organic-N was converted to NH_4^+ by ammonification, and NH_4^+ then converted to NO_x by nitrification. Compared to stormwater runoff from the P1 site, the PON concentrations decreased dramatically from 0.93 mg/L to 0.14 mg/L. The NH_4^+

concentrations demonstrated a significant reduction (from 0.15 mg/L to 0.07 mg/L) and the NO_x concentrations exhibited a sizeable increase (from 0.30 mg/L to 0.50 mg/L). The dissolved fractions in the raw water ($f_d = \frac{DN}{TN}$) increased from 43% to 84%, indicating good removal performance of PON. NO_x accounted for 68% of the DN, as compared to the stormwater runoff at 43%, illustrating the nitrification process at this stage.

In the second stage, the denitrification vaults provided enough detention time and anoxic conditions to promote denitrification, during which the NO_x could be converted to N_2O and N_2 gas. Significant decreases in NO_x between the paver effluent (0.50 mg/L) and vault water (0.15 mg/L) were observed. The NH_4^+ and PON were almost maintained at their respective levels, and a slight release of DON was found (an increase from 0.16 mg/L to 0.19 mg/L).

Compared to the P1 site, it was found that the porous pavement/denitrification treatment train had some merits: (i) the PON removal was better than at the P1 site (P1 = 0.26 mg/L, N1 = 0.13 mg/L), which indicated that the filtration function was quite strong; (ii) NO_3^- could be converted to gaseous species and be permanently removed, which was more effective than at the P1 site (P1 = 0.65 mg/L, N1 = 0.15 mg/L); and (iii) the leaching of DON was not as high as at the P1 site (P1 = 0.63 mg/L, N1 = 0.19 mg/L). As a result, N1 had obvious advantages in dealing with nitrogen.

Table 4-1 Comparison of the water quality and annual pollutant mass loads of N at the N1 and P1 sites.

	EMC (mg/L)[a]			
Pollutants	P1 Input[b]	P1 Output[b]	P1 Output[b]	N1 stage 2[d]
TN	1.62	1.55	0.87	0.56
PON	0.93	0.26	0.14	0.13
DON	0.25	0.63	0.16	0.19
NO_x	0.30	0.65	0.50	0.15
NH_4^+	0.15	< 0.05	0.07	0.08
	L (kg/ha-yr)			
Pollutants	P1 Input[b]	P1 Output[b]	P1 Output[b]	N1 stage 2[d]
TN	14.0	9.2	9.3	5.6
PON	8.0	1.3	1.5	1.3
DON	2.2	3.3	1.8	1.9
NO_x	2.5	3.5	5.3	1.6
NH_4^+	1.3	0.2	0.7	0.8

[a]Based on the cumulative mass divided by the cumulative volume for all collected samples.
[b]Data from the P1 site were collected by Li and Davis (2014).
[c]Porous pavement effluent at the enhanced N removal site.
[d]Infiltration water at the enhanced N removal site.

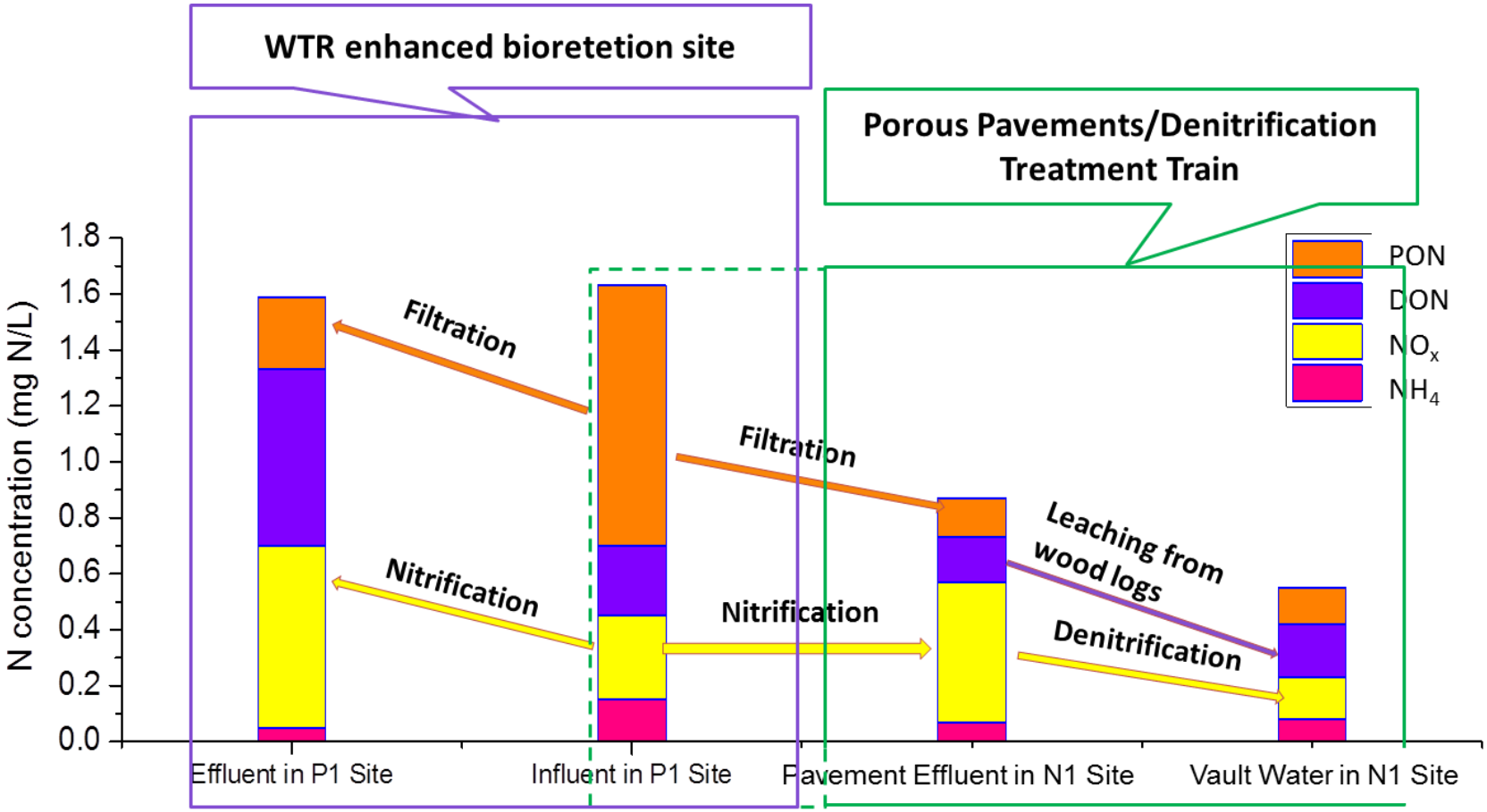


Figure 4-9 N composition at the enhanced N removal site (*influent and effluent data were obtained from the nearby P1 site (Li and Davis 2014)

4.3.4 Volume Balance and Mass Load Balance

Figure 4-10 shows the balances of both water volume and N mass loads at the N1 site. From August 1, 2013 to May 6, 2014, 52 storms were monitored. The total rainfall depth was approximately 68.8 cm, corresponding to 55 m^3 over the pavement. However, the depth cannot be accurately determined due to significant snow and other frozen precipitation. The assumed mass TN load was 14.0 kg/ha-yr, based on the nearby University of Maryland parking lot (P1) runoff (Li and Davis 2014).

The total water volume going to the vaults from the pavers was about 51.5 m^3, containing 9.3 kg/ha-yr TN. Since this porous pavement area is lined and does not allow percolation, all water lost (3.5 m^3) was assumed to be due to evapotranspiration, which would not result in any TN removal. Around 34% of the TN (4.7 kg/ha-yr) was held in the porous pavement.

PON and NH_4^+ reductions were 6.5 kg/ha-yr and 1.8 kg/ha-yr (Table 4-2), respectively, which indicated good performance with regards to infiltration and nitrification by the porous pavements. The 1.8 kg/ha-yr production of NO_x could be attributable to both the ammonification and nitrification processes (Li and Davis 2014). The slight increase in DON could be due to the conversion and leaching of organic matter in the media of the PON.

It is assumed that no effluent left the denitrification vaults from the discharge pipe. The total volume reduction was based on water leaking from the vaults into the ground, which resulted in a TN mass load reduction of 5.6 kg/ha-yr, accounting for 40% of the total mass load. From the volume balance and mass balance, the TN mass load reduction

by reactions in the denitrification vaults was 3.7 kg/ha-yr, around 26% of the total mass load, and almost entirely based on the mass load reduction of NO_x (3.8 kg/ha-yr). PON was reduced slightly, by 0.2 kg/ha-yr. The small amount of production of DON and NH_4^+ could be due to the leaching from the wood logs (Robertson 2010; Peterson 2013). As a result, the N mass reduction that occurred was not only due to volume reduction (40%), but also to system reaction (60%).

The inflow PON mass proportion of TN was 57.1%, and reduced to about 16.1% in the porous pavement effluent, then around 23.2% in the denitrification vault infiltration water, indicating the removal of TN in the porous pavement was dominated by particulate nitrogen, whereas in the denitrification vault removal was dominated by dissolved nitrogen (DN). Moreover the DON fractions of DN were 36.7%, 23.1% and 44.2% in the stormwater runoff, porous pavement effluents and denitrification vault infiltration waters, respectively, which was illustrate that nitrogen removal in the denitrification vault was dominated by the inorganic nitrogen.

Table 4-2 N mass loads in different stages at the enhanced N removal site.

	L (kg/ha-yr)				
	PON	DON	NO_x	NH_4^+	TN
Rainfall runoff*	8.0	2.2	1.3	2.5	14.0
Stage 1					
Evapotranspiration	0.0	0.0	0.0	0.0	0.0
Reactions in porous pavement	6.5	0.4	-4.0	1.8	4.7
Porous pavement effluent	1.5	1.8	5.3	0.7	9.3
Stage 2					
Infiltrating water	1.3	1.9	1.6	0.8	5.6
Reactions in denitrification vaults	0.2	-0.2	3.8	-0.1	3.7

*Data from the P1 site were collected by Li and Davis (2014).

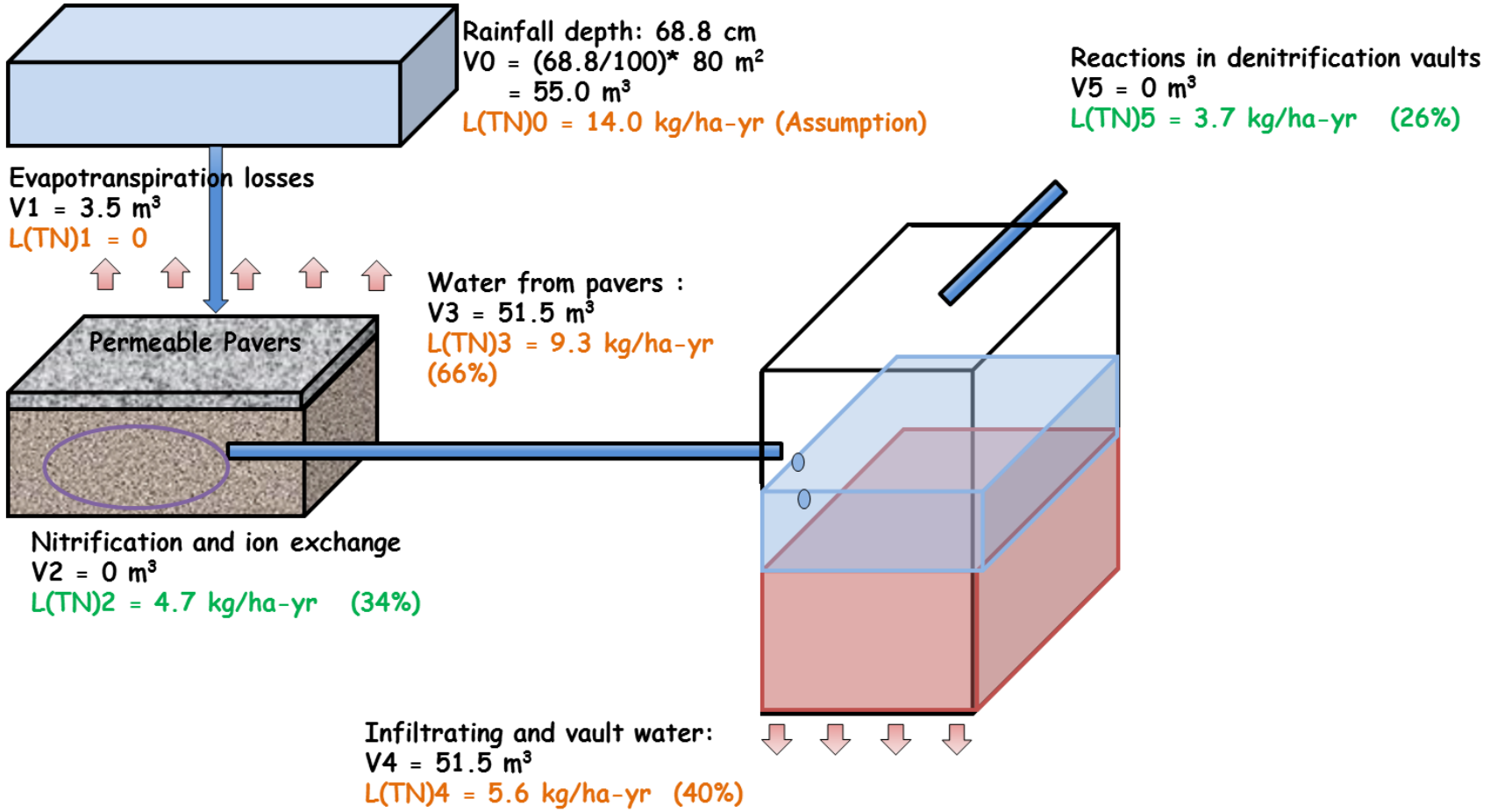


Figure 4-10 Volume and N mass load balances at the enhanced N removal site.

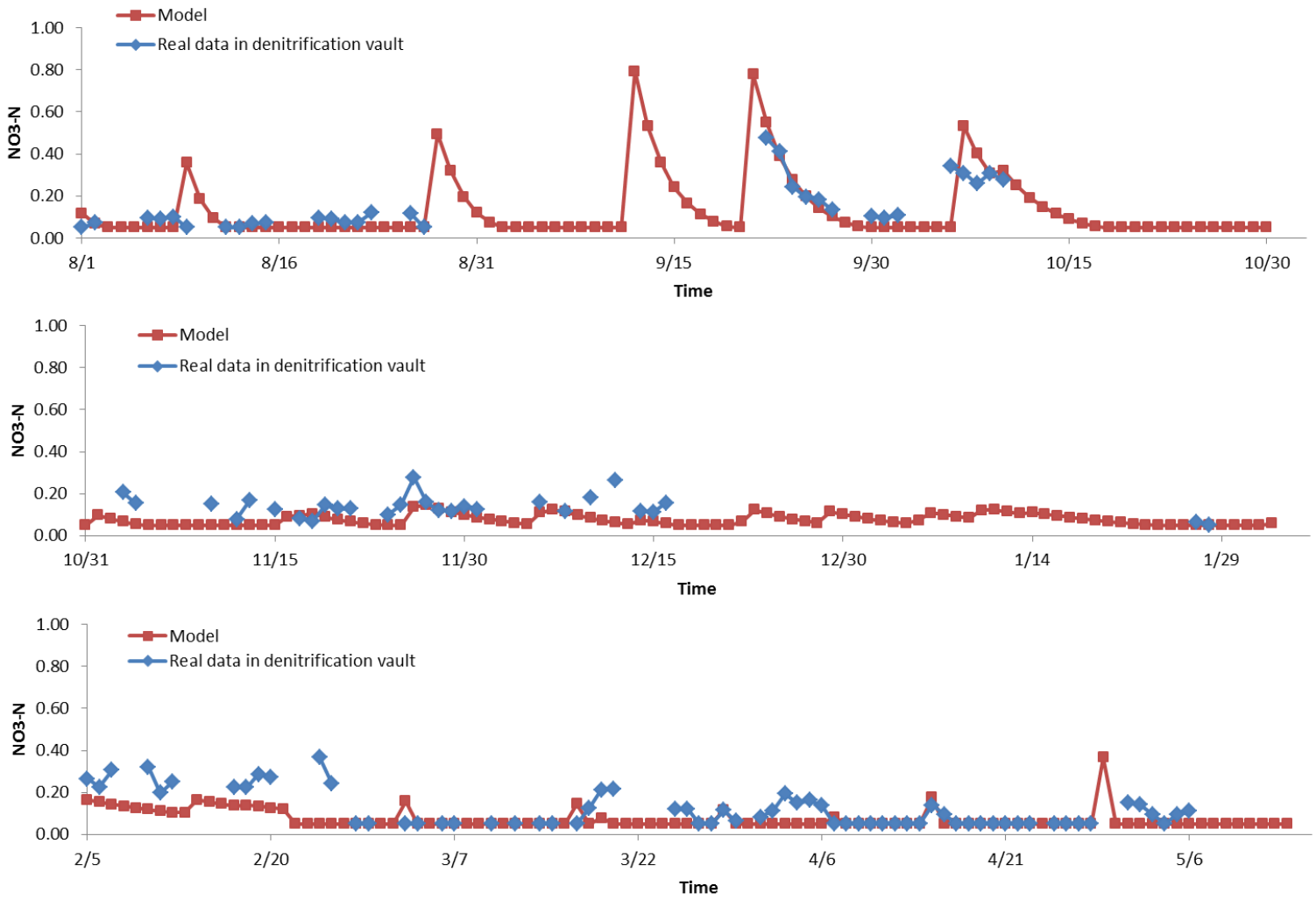


Figure 4-11 Fit of a first-order model to the NO_3^- concentrations of collected samples from the denitrification vault at the enhanced N removal site.

4.3.5 Nitrate removal in the Denitrification Vault

The denitrificaion process is described as a zero-order reaction in most wastewater studies, indicating the nitrate is not the limiting substrate. Robertson (2010) found the nitrate mass removal rate to be relatively constant at influent NO_3^- concentrations from 3.1 to 48.8 mg N /L and a zero-order model most accurately depicted the data. However, first-order kinetics may provide better fit for the denitrification process at low influent nitrate concentrations(Leverenz et al. 2010). In Peterson (2013)'s column research, the denitrification of artificial stormwater followed pseudo-first order kinetics with the highest nitrate removal percentage found at an average retention time of 0.8 day.

Since the typical EMCs of TN in urban storm events (land use) are approximately 1 to 3 mg/L (Collins et al. 2010), a first order kinetic model was used to describe the reactions in the denitrification vaults in this research. In order to simplify the model, some assumptions were made: The volume of water in the denitrification vault at the beginning of a day is recorded as V_o. If storm occurred that day, the volume of runoff and mass of pollutants were added to the system instantaneously and completely mixed. Water temperature has been recognized as an important parameter to affect denitrification rates (Bremner and Shaw 1958; Beauchamp et al. 1989). The first-order reaction and temperature-activity coefficient is given as (Metcalf 2003):

$$C = C^* \cdot e^{-k_T t} \qquad \textbf{Equation 4-1}$$

$$k_T = k_{20} \cdot \theta^{(T-20)} \qquad \textbf{Equation 4-2}$$

where T is temperature, °C; k_{20} is reaction-rate coefficient at 20 ℃; k_T is reaction-rate coefficient at T, ℃; Θ is the temperature-activity coefficient.

This model was fitted to the collected data using a least squares analysis and results are presented in Figure 4-11. The reaction-rate coefficient and the temperature-activity coefficient were used as fitting parameters. The nitrate removal was found to be well described by first-order kinetics during the running period except for data collected from December to February. This may due to the extremely low temperature and large amount of snow dissolve agent adding during that time, inhibiting the denitrificaiton process. The removal rate constant at 20℃ (k_{20}) was determined to be 1.05 d^{-1}, with the temperature coefficient (Θ) of 1.20, which are similar to those found by Leverenz et al. (2010) from their investigation in an unplanted experimental wood-chip media anoxic subsurface flow wetlands, k_{20} at 1.30 d-1 and Θ at 1.17.

4.4 Summary

This project demonstrated the capacity of the combination porous pavement/denitrification vault treatment train to reduce N loads. Regarding hydrology performance, flows could effectively be managed by the treatment train system, which achieved a near-zero discharge due to infiltration from the vaults during dry weather.

Results indicate that the treatment train performed well with regards to N removal and had obvious advantages over bioretention systems, also revealing the following mechanism for N removal in the treatment train: (1) porous pavers

exhibited good performance for filtration, nitrification, and possibly ion exchange. PON was filtered by the media under the porous pavers. The porous pavers provided the aerobic conditions necessary to drive nitrification, in which NH_4^+ and organic-N were converted to NO_x. Compared to the runoff from the nearby P1 bioretention site, the concentrations of PON and NH_4^+ were at low levels and NO_x was at a high level in the porous pavement effluent (P1 runoff: PON = 0.93 mg/L, NH_4^+ = 0.15 mg/L, NO_x = 0.30 mg/L; Porous pavements effluent: PON = 0.14 mg/L, NH_4^+ = 0.07 mg/L, NO_x = 0.50 mg/L). (2) Water in the denitrification vault underwent a short nitrification process when the porous paver effluent entered, and was retained for a short time (from a couple of hours up to one or two days), during which ORP increased and pH decreased. After that, the vaults provided enough detention time (approximately two days) and anoxic conditions (ORP was around -340 mV) to promote denitrification, during which the NO_x was converted to N_2O and N_2 gas. A large decrease in NOx concentration was found between the paver effluent (0.50 mg/L) and vault water (0.15 mg/L). Considering both volume balance and mass balance, the mass reduction results for N resulted not only because of volume reduction, but also due to system reactions.

Chapter 5: Conclusions and Recommendations

5.1 Conclusions

This project demonstrates novel technologies for lowering nutrient discharges to surface waters, improving water quality, and reducing discharge flows from urban stormwater runoff.

5.1.1 Bioretention Retrofit for Enhanced Phosphorus Removal: Hydrology and Water Quality

The P1 site was monitored from July 2011 to April 2013; 114 storm events were monitored. During 31 storm events, water quality data were collected. The sampled events patterns reasonably reflected the historical rainfall distributions from 2011 to 2013.

Aluminum-based water treatment residuals (WTR) incorporated into the bioretention system media resulted in excellent hydrologic performance. During the 114 monitored storms, 860 m^3 of stormwater was removed from the total 2,120 m^3 of runoff that entered the bioretention system, for a net reduction of 40%. Although the field-determined bioretention abstraction volume (BAV) was lower than the calculated BAV, indicating that the bioretention cell surface and media were not fully utilized, volume reduction was noted for more than 96% of the monitored storm events. Compared with before the WTR retrofit, the volume reduction ratios (f_v)

were significantly lower during the current study, indicating a better level of efficacy for flow management.

Total suspended solid (TSS), total phosphorus (TP) and particulate (PP) concentrations in runoff inflow were significantly reduced (as compared to outflow) due to the filtration of particulate matter. The bioretention discharge met the 25 mg/L TSS target level criterion (Davis and McCuen 2005) 92% (83.6 hr out of 90.5 hr) of the discharge time, compared to only 9% (6.61 hr out of 70.84 hr) for the influent, which matched well with results obtained before the WTR retrofit. This demonstrated that WTR incorporation did not harm the filtration performance of the bioretention media. TP export was found during the previous study (EMCs: input median = 0.14 mg/L, output median = 0.32 mg/L) (Li and Davis 2009), whereas the media was shown to be effective for treating TP in the current study (EMCs: input median = 0.31 mg/L, output median = 0.11 mg/L), which is attributable to the increase of P adsorption capacity contributed by the WTR (Dayton and Basta 2005a; Novak and Watts 2005; O'Neill and Davis 2012a; O'Neill and Davis 2012b). Although the net removal of soluble reactive phosphorus (SRP) and dissolve organic phosphorus (DOP) from the incoming runoff was not found, leaching of dissolved phosphorus (DP) was prevented not only from the incoming runoff, but also from the media and captured PP. The near constant SRP and DOP outflow concentrations suggested an equilibrium adsorption treatment mechanism.

Mass loads were reduced for TSS and all P species. The pollutant mass removal levels were higher than the event mean concentration (EMC) removal levels, due to the attenuation of volume by the bioretention media.

5.1.2 Bioretention Retrofit for Enhanced Phosphorus Removal: Media Performance

WTR is slightly acidic (pH = 6.5); it was found in various shapes and sizes and to be highly porous. The high amount of amorphous Al and Fe (Al_{ox} + Fe_{ox}) and low amount of water extractable phosphorus (WEP) was an indication of the high sorption capacity and low leaching potential of P (McLaughlin et al. 1981; Elliott et al. 2002).

Media samples were collected before WTR incorporation, and then every four to six months thereafter. The media texture was not modified by the WTR addition; however, pH decreased slightly from 7.3 to 6.8. The amount of amorphous aluminum and iron (Al_{ox} + Fe_{ox}) at the P1 site dramatically increased after the WTR retrofit, especially for Al_{ox} (from approximately 11 mmol/kg to approximately 77 mmol /kg). This resulted in an apparent PSI decrease from approximately 0.075 to approximately 0.041. This implied that the P sorption capacity was enhanced by the WTR addition (Kleinman et al. 2000; Agyin-Birikorang and O'Connor 2007).

P distribution in the bioretention media had a strong correlation with the runoff pathway in the cell. Higher concentrations were found in the top media and closer to the runoff inlet. Before adding the WTR, P sorption capacity decreased from the top layer of media to the lower layers of media before the WTR amendment, which may be attributable to the fact that most of the amorphous Al and Fe were brought by runoff and accumulated in the surface media. However, the P sorption capacity was extended in the lower media after WTR retrofit, and the PSI values did not change significantly afterwards. The phosphorus saturation index (PSI) remained

below 0.05 during the two year study period, which implies good P sorption capacity for long term operation.

Mass balance calculations were analyzed using the data from the water quality monitoring; they indicated that the media P kept increasing during the study period, mostly due to input from stormwater runoff. However, the media accumulated P mass in the spring was lower than in the fall, which may have been due to plant growth activity.

In a laboratory investigation, captured PP leached DP during successive wet/dry events, when water entered at a dissolved organic fraction ($f_{d\text{-}org}$) of approximately 67%. Comparing the output EMCs of SRP (0.037 mg/L) and DOP (0.028 mg/L) at the P1 site, it can be concluded that WTR addition enhanced the sorption capacity for DOP as well as SRP, and finally achieved enhanced P removal for urban stormwater; thus, this is a feasible method for traditional bioretention media refinement.

5.1.3 Porous Pavement/Denitrification Vault Treatment Train for Enhanced Nitrogen Removal

The N1 site was monitored from August 2013 to May 2014; water quality data were collected for 21 storm events and 165 grab samples from the denitrification vaults.

In terms of hydrologic performance, flows can be managed effectively by the treatment train system, which nearly achieved zero discharge due to combination of

captured water evaporation in the porous pavement and infiltration from the vaults during dry weather.

The porous pavements worked as a filter removing most of the particulate matter and providing aerobic conditions to drive nitrification; under such conditions the NH_4^+ and organic N were converted to NO_x between the storm events (Davis et al. 2001; Hsieh and Davis 2005; Cho et al. 2009). NO_x was washed from the media of the porous pavement and transferred to stored water in the denitrification vault during the storm events. The function at this stage was similar to that of a bioretention site without the vegetation planted. Compared to stormwater runoff from the P1 site (Li and Davis 2014), the concentrations of PON and NH_4^+ were at low levels and NO_x was at a high level (P1 runoff: PON = 0.93 mg/L, NH_4^+ = 0.15 mg/L, NO_x = 0.30 mg/L; Porous pavements effluent: PON = 0.14 mg/L, NH_4^+ = 0.07 mg/L, NO_x = 0.50 mg/L).

The water in the denitrification vaults underwent a short nitrification process when the porous paver effluent entered and was retained for a short amount of time (from a couple to dozens of hours; ORP increased to around 100 mV, pH decreased to around 7.2), depending amount the duration of the rainfall. After that, the vaults provided enough detention time (approximately two days) and anoxic conditions (ORP was around -340 mV, pH was around 8) to promote denitrification, during which the NO_x was converted to nitrogen gases. A large decrease in NO_x concentration was found between the paver effluent (0.50 mg/L) and vault water (0.15 mg/L), indicating the denitrification process.

Considering both volume and mass balances, in the porous pavement, approximately 34% of TN (4.7 kg/ha-yr) was mitigated by filtration processes; 6.5 kg/ha-yr of PON and 1.8 kg/ha-yr of NH_4^+ were removed, and 4.0 kg/ha-yr of NO_x were created. In the denitrification vaults, about 26% of TN (3.7 kg/ha-yr) was decreased by system reaction, mostly due to the decrease of NO_x (3.8 kg/ha-yr). PON was reduced slightly, by 0.2 kg/ha-yr. The small amount of production of DON and NH_4^+ could be due to leaching from the wood logs (Robertson 2010; Peterson 2013). In summary, the N mass reduction that occurred was not only due to volume reduction, but also to system reaction (60%).

Compared with the WTR-enhanced P removal bioretention site, the porous pavement/denitrification treatment train has certain advantages for N removal. PON removal was as good, or even better, than at the bioretention site (P1 = 0.26 mg/L, N1 = 0.13 mg/L), which indicated that the filtration function was quite strong. The NO_3^- could finally be converted to gas and be permanently removed, which was more effective than at the P1 site (P1 = 0.65 mg/L, N1 = 0.15 mg/L). Finally, the leaching of DON was not as high as at the P1 site (P1 = 0.63 mg/L, N1 = 0.19 mg/L).

5.2 Recommendations

In the enhanced P removal bioretention site, the field-determined BAV of 6.88 m^3 was much lower than the calculated average BAV (38.2 m^3), indicating that the bioretention cell was not fully utilized. This is attributable to the multidimensional flow mentioned by Davis et al. (2012), wherein underdrain flow was initiated in the area near the flow inlet; much less of the hydraulic load was transferred to the media

further away from the outlet during larger events. The cell had a sloped surface before WTR amendment in order to encourage runoff coming into the cell to migrate as far as possible away from the inlet. However, the retrofit work may have modified the media slope. Moreover, measurements indicated that the P distribution in the media had a strong correlation with the runoff path. Higher concentrations were found in the surface media close to the runoff inlet. Two recommendations can be made for further traditional bioretention cells with WTR retrofitting: (i) WTR incorporation should be applied only to the area closest to the runoff inlet instead of to the entire bioretention cell, which will significantly reduce construction costs and the amount of work required to increase the feasibility of bioretention refinements; (ii) the surface slopes should be recreated during the retrofit.

In the porous pavement/denitrification vault treatment train, flows could be managed effectively by the treatment train system, which achieved nearly zero discharge due to infiltration from the vaults during dry weather. As a result, a higher drainage area should be applied for the vault size used. Moreover, the function of porous pavement is to remove particulate matter and provide aerobic conditions to drive nitrification, a function similar to that of a traditional bioretention cell. The traditional bioretention cell can be modified by adding denitrification vaults in order to achieve enhanced N removal.

SRP and DOP existed at nearly equal fractions of DP in the incoming runoff, whereas SRP accounted for 59% of DP in the effluent. Moreover, as mentioned above, DOP leaching from captured PP and microbial processes appear to be occurring in the media (Scarlatos 1997; Chen and Sheng 2005; Berretta and Sansalone 2012). This

suggests that WTRs have the ability to sorb DOP. The reason for the slight change in DON in the treatment train was not completely clarified. Further attention should be paid to these organic forms of the nutrients, for which theories and models need to be improved. Long-term and seasonal performances of these novel SCMS should also be evaluated.

Appendix 1: Hydrological Data for Enhanced P Removal Bioretention Site

Date	Rainfall Depth	Rainfall Duration	Rainfall Intensity	V_{in}	V_{out}	f_v
	cm	hour	cm/hr	m^3	m^3	
8-Jul-11	0.864	2.300	0.375	8.699	5.672	0.652
13-Jul-11	0.203	0.300	0.677	2.308	0.063	0.027
19-Jul-11	0.330	0.100	3.302	2.899	0.000	0.000
25-Jul-11	0.559	3.867	0.145	6.956	0.017	0.002
1-Aug-11	1.454	0.300	4.847	17.778	3.151	0.177
6-Aug-11	0.984	2.767	0.356	9.265	4.755	0.513
7-Aug-11	0.425	0.200	2.127	4.874	3.058	0.627
13-Aug-11	1.270	3.400	0.374	13.597	7.521	0.553
13-Aug-11	5.798	19.500	0.297	47.747	84.798	1.776
18-Aug-11	0.279	9.267	0.030	4.974	0.023	0.005
21-Aug-11	2.223	2.667	0.833	19.520	19.451	0.996
25-Aug-11	0.737	4.433	0.166	9.320	4.064	0.436
27-Aug-11	9.754	22.067	0.442	223.337	208.037	0.931
2-Sep-11	2.018			16.950	0.182	0.011
3-Sep-11	0.279	0.167	1.676	4.311	1.502	0.348
5-Sep-11	3.302	9.433	0.350	46.432	38.040	0.819
6-Sep-11	1.092	16.167	0.068	22.632	14.649	0.647
7-Sep-11	9.823	26.400	0.372	135.291	157.278	1.163
8-Sep-11	2.261	8.700	0.260	53.695	45.757	0.852
15-Sep-11	0.203	2.333	0.087	2.984	0.000	0.000
20-Sep-11	0.229	3.400	0.067	4.123	0.000	0.000
23-Sep-11	2.515	8.367	0.301	36.806	26.100	0.709
28-Sep-11	0.559	1.267	0.441	7.215	5.391	0.747
28-Sep-11	0.800	1.633	0.490	12.204	12.204	1.000
1-Oct-11	0.686	8.867	0.077	10.157	6.177	0.608
12-Oct-11	3.547	48.300	0.073	41.684	34.695	0.832
19-Oct-11	1.473	19.033	0.077	27.642	13.191	0.477
26-Oct-11	0.356	1.867	0.191	4.648	0.386	0.083
27-Oct-11	0.432	10.500	0.041	5.446	2.904	0.533
28-Oct-11	2.819	20.433	0.138	63.212	33.482	0.530
10-Nov-11	0.178	1.863	0.095	1.863	0.000	0.000
16-Nov-11	0.864	22.700	0.038	8.306	1.759	0.212

Date	Rainfall Depth	Rainfall Duration	Rainfall Intensity	V_{in}	V_{out}	f_v
	cm	hour	cm/hr	m^3	m^3	
20-Nov-11	0.305	4.133	0.074	4.166	N/A	N/A
29-Nov-11	0.940	12.200	0.077	21.810	7.306	0.335
6-Dec-11	7.417	44.467	0.167	115.911	51.135	0.441
21-Dec-11	0.127	4.267	0.030	1.474	0.000	0.000
21-Jan-12	0.610	6.567	0.093	5.894	0.000	0.000
27-Jan-12	0.762	1.700	0.448	6.879	0.000	0.000
1-Feb-12	0.102	0.867	0.117	1.507	0.000	0.000
8-Feb-12	0.203	4.100	0.050	2.756	0.000	0.000
11-Feb-12	0.279	7.000	0.040	4.787	0.000	0.000
16-Feb-12	0.254	5.733	0.044	4.584	0.000	0.000
24-Feb-12	0.813	3.667	0.222	9.839	0.021	0.002
29-Feb-12	3.531	22.467	0.157	49.662	20.023	0.403
2-Mar-12	1.727	16.600	0.104	29.202	18.632	0.638
9-Mar-12	0.025	0.033	0.762	0.280	0.000	0.000
20-Mar-12	0.787	3.333	0.236	10.838	1.556	0.144
24-Mar-12	0.762	21.967	0.035	9.912	4.361	0.440
2-Apr-12	0.152	1.800	0.085	2.198	0.000	0.000
21-Apr-12	0.229	1.233	0.185	2.441	0.000	0.000
22-Apr-12	2.997	11.667	0.257	54.966	21.056	0.383
26-Apr-12	0.025	0.033	0.762	0.210	0.000	0.000
28-Apr-12	0.953	7.067	0.135	10.817	0.000	0.000
1-May-12	0.279	1.200	0.233	6.003	0.000	0.000
8-May-12	0.152	13.067	0.012	2.286	0.000	0.000
9-May-12	1.016	7.433	0.137	21.296	3.468	0.163
14-May-12	2.083	65.467	0.032	34.913	12.370	0.354
20-May-12	0.762	33.633	0.023	7.934	1.481	0.187
27-May-12	0.127	3.333	0.038	1.909	0.000	0.000
29-May-12	0.940	8.500	0.111	9.087	0.080	0.009
29-Jun-12	1.797	2.367	0.759	15.360	3.465	0.226
9-Jul-12	0.432	6.100	0.071	6.050	0.000	0.000
10-Jul-12	0.940	2.933	0.320	14.972	0.001	0.000
14-Jul-12	0.876	2.800	0.313	9.621	1.238	0.129
18-Jul-12	1.041	0.700	1.488	16.129	3.300	0.205
19-Jul-12	2.527	3.500	0.722	32.190	15.951	0.496
20-Jul-12	2.718	39.802	0.068	42.046	27.654	0.658

Date	Rainfall Depth	Rainfall Duration	Rainfall Intensity	V_{in}	V_{out}	f_v
	cm	hour	cm/hr	m^3	m^3	
26-Jul-12	0.102	0.167	0.610	1.554	0.000	0.000
31-Jul-12	0.152	0.233	0.653	1.990	0.000	0.000
2-Aug-12	0.425	0.333	1.276	5.449	0.000	0.000
5-Aug-12	0.406	2.167	0.188	5.068	0.000	0.000
10-Aug-12	1.575	3.433	0.459	24.067	4.308	0.179
11-Aug-12	0.127	0.800	0.159	2.235	0.024	0.011
11-Aug-12	0.305	1.400	0.218	5.585	3.250	0.582
14-Aug-12	0.152	1.067	0.143	1.752	0.000	0.000
17-Aug-12	0.889	5.533	0.161	15.266	0.537	0.035
19-Aug-12	0.152	1.767	0.086	1.925	0.000	0.000
20-Aug-12	0.660	0.667	0.991	9.406	2.601	0.277
21-Aug-12	0.203	0.133	1.524	2.409	0.421	0.175
25-Aug-12	0.051	0.400	0.127	0.775	0.000	0.000
26-Aug-12	0.933	4.400	0.212	12.873	2.100	0.163
28-Aug-12	0.076	0.733	0.104	1.054	0.000	0.000
1-Sep-12	0.737	2.000	0.368	8.243	0.455	0.055
2-Sep-12	0.152	0.133	1.143	2.042	0.000	0.000
6-Sep-12	0.178	1.967	0.090	2.333	0.000	0.000
8-Sep-12	1.911	1.400	1.365	23.188	9.407	0.406
18-Sep-12	0.737	1.833	0.402	10.404	0.011	0.001
18-Sep-12	0.940	3.667	0.256	19.325	9.492	0.491
26-Sep-12	0.152	0.767	0.199	2.065	0.000	0.000
27-Sep-12	1.321	7.533	0.175	18.291	2.975	0.163
30-Sep-12	0.076	1.167	0.065	1.205	0.000	0.000
2-Oct-12	1.499	4.033	0.372	16.129	9.634	0.597
4-Oct-12	0.025	0.033	0.762	0.226	0.000	0.000
7-Oct-12	0.152	1.967	0.077	2.517	0.000	0.000
7-Oct-12	0.279	2.100	0.133	3.487	0.000	0.000
9-Oct-12	0.305	4.000	0.076	4.137	0.000	0.000
15-Oct-12	0.102	1.167	0.087	1.124	0.000	0.000
19-Oct-12	0.102	0.100	1.016	1.138	0.000	0.000
19-Oct-12	0.387	0.733	0.528	4.875	0.001	0.000
19-Oct-12	1.664	14.533	0.114	16.017	10.978	0.685
28-Oct-12	12.522	50.933	0.246	209.277	176.903	0.845
7-Nov-12	0.127	1.667	0.076	2.093	0.000	0.000

Date	Rainfall Depth	Rainfall Duration	Rainfall Intensity	V_{in}	V_{out}	f_v
	cm	hour	cm/hr	m^3	m^3	
13-Nov-12	1.270	9.500	0.134	26.868	5.828	0.217
30-Jan-13	3.194	6.300	0.507	56.136	39.672	0.707
8-Feb-13	0.406	9.667	0.042	9.432	0.000	0.000
11-Feb-13	0.711	5.167	0.138	17.483	5.315	0.304
13-Feb-13	0.559	5.400	0.103	13.180	4.695	0.356
15-Feb-13	0.330	3.133	0.105	8.025	2.610	0.325
19-Feb-13	0.152	1.667	0.091	3.775	0.000	0.000
26-Feb-13	1.321	16.667	0.079	30.292	14.327	0.473
11-Mar-13	1.740	6.500	0.268	25.088	18.230	0.727
17-Mar-13	0.762	5.300	0.144	14.101	1.725	0.122
3-Apr-13	0.610	10.833	0.056	9.885	0.000	0.000
11-Apr-13	1.219	4.100	0.297	14.267	6.623	0.464

Appendix 2: Water Data for Enhanced P Removal Bioretention Site

1. Sample Based Summary for P species and TSS.

	In							Out						
	Time	TP	TDP	SRP	PP	DOP	TSS	Time	TP	TDP	SRP	PP	DOP	TSS
		mg/L	mg/L	mg/L	mg/L	mg/L	mg/L		mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
2011	7/31 17:27	0.76	0.03		0.73		649.8	7/31 17:57	0.19	0.04		0.15		34.6
	7/31 17:47	0.12	0.03		0.09		24.2	7/31 18:17	0.16	0.10		0.06		9.4
								7/31 18:37	0.15	0.07		0.08		5.2
								7/31 18:57	0.15	0.09		0.06		3.8
								7/31 19:17	0.15	0.09		0.05		0.8
								7/31 19:57	0.16	0.08		0.07		0.5
	8/5 17:37	0.27	0.04		0.23		269.0	8/5 18:09	0.12	0.08		0.03		31.6
	8/5 17:57	0.06	0.03		0.03		13.6	8/5 18:29	0.11	0.08		0.04		20.8
	8/5 18:37	0.04	0.03		0.02		32.6	8/5 18:49	0.10	0.08		0.02		6.6
	8/5 18:57	0.08	0.03		0.05			8/5 19:09	0.11	0.09		0.02		5.4
								8/5 19:29	0.10	0.08		0.02		3.6
								8/5 20:09	0.11	0.08		0.03		3.2
								8/5 20:49	0.11	0.09		0.02		2.6
								8/5 21:29	0.11	0.09		0.03		2.4
								8/5 22:29	0.12	0.09		0.03		3.0
								8/5 23:29	0.12	0.09		0.03		3.2
								8/6 0:29	0.12	0.09		0.03		4.8
								8/6 2:09	0.11	0.09		0.03		4.4

	In							Out						
	Time	TP	TDP	SRP	PP	DOP	TSS	Time	TP	TDP	SRP	PP	DOP	TSS
		mg/L	mg/L	mg/L	mg/L	mg/L	mg/L		mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
	8/12 13:35	0.29	0.06		0.23		218.8	8/12 16:59	0.19	0.09		0.10		15.8
	8/12 13:55	0.15	0.05		0.09		27.4	8/12 17:19	0.15	0.11		0.04		2.0
								8/12 17:39	0.14	0.11		0.03		1.4
								8/12 17:59	0.14	0.11		0.03		0.6
								8/12 18:19	0.14	0.11		0.03		9.0
								8/12 18:59	0.13	0.11		0.02		0.5
								8/12 19:39	0.14	0.11		0.03		7.4
								8/12 20:19	0.12	0.10		0.03		1.2
								8/12 21:19	0.13	0.10		0.03		2.0
								8/12 22:19	0.13	0.10		0.03		2.0
								8/12 23:19	0.13	0.11		0.02		4.8
								8/13 0:59	0.12	0.10		0.02		4.6

	In							Out						
	Time	TP	TDP	SRP	PP	DOP	TSS	Time	TP	TDP	SRP	PP	DOP	TSS
		mg/L	mg/L	mg/L	mg/L	mg/L	mg/L		mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
	8/26 11:31	0.55	0.04		0.51		430.4	8/26 13:19	0.08	0.04		0.04		5.6
	8/26 11:51	0.16	0.06		0.10		19.8	8/26 13:39	0.07	0.05		0.02		4.0
	8/26 12:11	0.16	0.05		0.11		44.0	8/26 13:59	0.07	0.05		0.02		3.0
	8/26 12:31	0.28	0.04		0.24			8/26 14:19	0.07	0.05		0.01		3.0
	8/26 12:51	0.09	0.02		0.07		22.2	8/26 14:39	0.07	0.05		0.02		2.8
	8/26 13:11	0.13	0.03		0.10		28.4	8/26 15:19	0.07	0.06		0.01		2.0
	8/26 13:31	0.08	0.04		0.05		24.4	8/26 15:59	0.09	0.07		0.02		1.2
	8/26 14:11	0.10	0.03		0.07		50.6	8/26 16:39	0.10	0.07		0.03		1.0
	8/26 15:11	0.10	0.04		0.06		69.8	8/26 17:39	0.13	0.09		0.03		2.2
	8/26 16:11	0.11	0.03		0.08		62.4	8/26 18:39	0.13	0.10		0.03		0.5
	8/26 17:31	0.18	0.15		0.03		37.8	8/26 19:39	0.10	0.07		0.03		0.5
								8/26 21:19	0.11					
	9/1 3:03	0.87	0.23		0.64		173.4							
	9/1 3:23	0.30	0.16		0.14		35.6							
	9/2 11:13	0.14	0.05		0.09		53.8							
	9/2 11:33	0.13	0.08		0.06		17.2							

	In							Out						
	Time	TP	TDP	SRP	PP	DOP	TSS	Time	TP	TDP	SRP	PP	DOP	TSS
		mg/L	mg/L	mg/L	mg/L	mg/L	mg/L		mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
								9/4 18:17	0.08	0.04		0.05		7.0
								9/4 18:37	0.08	0.06		0.02		4.0
								9/4 18:57	0.09	0.07		0.02		4.4
								9/4 19:17	0.09	0.08		0.02		1.2
								9/4 19:37	0.09	0.07		0.02		4.0
								9/4 20:17	0.09	0.08		0.01		4.8
								9/4 20:57	0.08	0.07		0.01		4.4
								9/4 21:37	0.09	0.07		0.02		0.8
								9/4 22:37	0.08	0.07		0.01		3.4
								9/4 23:37	0.07	0.06		0.00		1.0
								9/5 0:37	0.08	0.07		0.01		0.5
								9/5 2:17		0.09				0.6
	9/14 15:25	0.57	0.20		0.38		164.5							
	9/14 15:45	0.32	0.21		0.11		129.6							
	9/14 16:05	0.24	0.05		0.19		43.5							

	In							Out						
	Time	TP	TDP	SRP	PP	DOP	TSS	Time	TP	TDP	SRP	PP	DOP	TSS
		mg/L	mg/L	mg/L	mg/L	mg/L	mg/L		mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
	9/22 11:10	0.37	0.05		0.32		177.9	9/22 12:05	0.07	0.03		0.04		18.9
	9/22 11:30	0.30	0.06		0.24		154.5	9/22 12:25	0.12	0.07		0.05		6.4
	9/22 11:50	0.30	0.03		0.27		304.3	9/22 12:45	0.13	0.08		0.05		4.3
	9/22 12:10	0.11	0.05		0.06		45.1	9/22 13:05	0.12	0.09		0.03		1.8
	9/22 12:30	0.10	0.04		0.06		46.4	9/22 13:25	0.11	0.09		0.02		2.9
	9/22 13:10	0.11	0.05		0.06		16.6	9/22 13:45		0.09				2.2
	9/22 13:30	0.08	0.06		0.02		25.4	9/22 14:05	0.09	0.06		0.03		2.4
	9/22 13:50	0.07	0.05		0.02		5.3	9/22 14:45	0.10	0.08		0.02		5.6
	9/22 14:50	0.08	0.03		0.05		34.8	9/22 15:25	0.09	0.07		0.03		1.3
	9/22 15:50	0.10	0.04		0.07		41.7	9/22 16:25	0.09	0.06		0.03		1.7
								9/22 17:25	0.10	0.07		0.03		1.6
								9/22 20:05	0.11	0.08		0.03		1.9
	10/25 13:07	0.67	0.22	0.14	0.44	0.08	270.0							
	10/25 13:27	0.32	0.11	0.08	0.20	0.03	224.9							
	10/25 13:47	0.28	0.11	0.07	0.17	0.04	159.2							
	10/25 14:07	0.22	0.11	0.06	0.12	0.04	54.3							
	10/25 14:27	0.34	0.10	0.07	0.24	0.03	116.9							
	10/25 14:47	0.21	0.06	0.04	0.15	0.02	88.7							
	10/25 15:07	0.18	0.08	0.05	0.10	0.03	63.5							
	10/25 15:27	0.20	0.09	0.06	0.11	0.03	91.3							

	In							Out						
	Time	TP	TDP	SRP	PP	DOP	TSS	Time	TP	TDP	SRP	PP	DOP	TSS
		mg/L	mg/L	mg/L	mg/L	mg/L	mg/L		mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
	11/9 16:39	0.99	0.38	0.25	0.60	0.13	327.0							
	11/9 16:59	0.58	0.25	0.16	0.33	0.09	126.9							
	11/9 17:19	0.57	0.27	0.19	0.30	0.09	83.7							
	11/9 17:59	0.48	0.16	0.11	0.32	0.05	72.7							
	11/9 17:39						118.9							
	11/9 18:19	0.39	0.15	0.10	0.24	0.05	83.7							
	11/9 18:39	0.35	0.15	0.10	0.20	0.04	66.3							
	11/9 18:59	0.43	0.17	0.12	0.26	0.05	60.3							
	11/9 19:19	0.39	0.20	0.14	0.18	0.06	55.5							
	11/15 2:21	0.81	0.37	0.31	0.44	0.06	86.5							
	11/15 2:41	0.45	0.22	0.19	0.23	0.02	31.5							
	11/15 3:01	0.48	0.28	0.24	0.20	0.05	23.4							
	11/15 3:21	0.66	0.43	0.38	0.23	0.05	22.4							
	11/15 3:41	0.67	0.44	0.41	0.23	0.03	24.3							

	In							Out						
	Time	TP	TDP	SRP	PP	DOP	TSS	Time	TP	TDP	SRP	PP	DOP	TSS
		mg/L	mg/L	mg/L	mg/L	mg/L	mg/L		mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
2012	1/31 6:59	0.38	0.04		0.34		141.2							
	1/31 7:19	0.33	0.03		0.30		175.5							
	1/31 7:39	0.21	0.03		0.18		77.8							
	1/31 7:59	0.18	0.03		0.14		37.6							
	1/31 8:19	0.17	0.03		0.14		31.9							
	1/31 8:39	0.17	0.03		0.14		41.9							
	1/31 8:59	0.14	0.03		0.11		44.0							
	2/7 17:19	0.45	0.15	0.02	0.30	0.12	181.8							
	2/7 17:39	0.40	0.06	0.03	0.34	0.03	180.5							
	2/7 17:59	0.34	0.04	0.02	0.30	0.02	175.5							
	2/7 18:19	0.28	0.04	0.02	0.24	0.02	123.7							
	2/7 18:39	0.25	0.04	0.02	0.21	0.02	78.3							
	2/7 18:59	0.22	0.05	0.02	0.18	0.02	59.8							
	2/7 19:19	0.24	0.04	0.02	0.20	0.02	62.7							
	2/7 19:39	0.21	0.04				49.4							
	2/7 19:59	0.17	0.04				36.8							
	2/7 20:59	0.14	0.04				27.1							

	In							Out						
	Time	TP	TDP	SRP	PP	DOP	TSS	Time	TP	TDP	SRP	PP	DOP	TSS
		mg/L	mg/L	mg/L	mg/L	mg/L	mg/L		mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
	3/1 17:05	1.22	0.08		1.14		562.2	3/2 0:51	0.13	0.01		0.13		40.7
	3/1 17:25	0.45	0.01		0.44		268.2	3/2 1:11	0.11	0.03		0.07		28.5
	3/1 17:45	0.59	0.01		0.58		433.9	3/2 1:31	0.14	0.01		0.13		
	3/1 18:05	0.61	0.10		0.51		243.8	3/2 1:51	0.10	0.03		0.08		18.5
	3/1 18:25	0.16	0.02		0.15		99.8	3/2 2:11	0.07	0.06		0.02		4.6
	3/1 18:45	0.16	0.02		0.15		76.5	3/2 2:51	0.09	0.05		0.03		1.4
	3/1 19:05	0.17	0.01		0.16		71.1	3/2 3:31	0.10	0.06		0.04		2.5
	3/1 19:25	0.21	0.02		0.19		76.0	3/2 4:11	0.09	0.05		0.03		1.6
	3/1 19:45	0.20	0.02		0.18		67.8	3/2 5:11	0.09	0.05		0.04		
	3/1 20:45	0.21	0.03		0.17		47.9	3/2 6:11	0.08	0.06		0.03		2.8
	3/1 21:45	0.15	0.02		0.12		44.2	3/2 7:11	0.08	0.06		0.03		1.0
	3/1 23:05	0.21	0.03		0.18		44.9	3/2 8:51	0.09	0.07		0.02		
	4/27 18:14	0.60	0.13	0.06	0.47	0.07	187.4							
	4/27 18:34	0.34	0.08	0.03	0.26	0.05	142.2							
	4/27 18:54	0.26	0.09	0.02	0.17	0.07	89.7							
	4/27 19:14	0.23	0.10	0.03	0.13	0.06	64.4							
	4/27 19:34	0.28	0.10	0.04	0.18	0.06	93.7							

	In							Out						
	Time	TP	TDP	SRP	PP	DOP	TSS	Time	TP	TDP	SRP	PP	DOP	TSS
		mg/L	mg/L	mg/L	mg/L	mg/L	mg/L		mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
	4/30 6:23	0.25	0.09	0.03	0.17	0.06	63.6							
	4/30 6:43	0.32	0.05	0.01	0.27	0.03	213.3							
	4/30 7:03	0.34	0.03	0.01	0.32	0.02	281.8							
	4/30 7:23	0.10	0.02	0.01	0.08	0.01	63.9							
	4/30 7:43	0.08	0.03	0.01	0.05	0.02	27.6							
	4/30 8:03	0.08	0.03	0.01	0.05	0.02	18.3							
	4/30 8:23	0.08	0.03	0.02	0.05	0.02	22.3							
	4/30 8:43	0.09	0.03	0.01	0.06	0.02	18.3							
	5/7 14:43	0.74	0.37	0.23	0.37	0.14	105.6							
	5/7 15:03	0.64	0.26	0.16	0.38	0.10	89.2							
	5/7 15:23	0.44	0.17	0.10	0.27	0.07	76.7							
	5/7 15:43	0.19	0.19	0.11	0.01	0.08	41.3							
	5/7 16:03	0.48	0.20	0.12	0.28	0.08	37.1							

	In							Out						
	Time	TP	TDP	SRP	PP	DOP	TSS	Time	TP	TDP	SRP	PP	DOP	TSS
		mg/L	mg/L	mg/L	mg/L	mg/L	mg/L		mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
	5/8 19:07	0.78	0.08	0.01	0.70	0.07	335.2							
	5/8 19:27	0.33	0.03		0.30		390.9							
	5/8 19:47	0.65					265.6							
	5/8 20:07	0.20	0.03	0.02	0.17	0.01	197.1							
	5/8 20:27	0.18	0.03	0.01	0.16	0.01	194.2							
	5/8 20:47	0.17	0.02	0.01	0.14	0.01	166.1							
	5/8 21:07	0.18	0.02	0.01	0.16	0.01	118.2							
	5/8 21:27	0.22	0.03	0.02	0.19	0.01	156.0							
	5/8 21:47	0.26	0.02	0.01	0.24	0.01	319.0							
	5/8 22:47	0.13					120.5							
	5/8 23:47	0.13	0.03		0.11		64.8							
	5/9 1:07	0.16	0.04		0.12		50.1							

	In							Out						
	Time	TP	TDP	SRP	PP	DOP	TSS	Time	TP	TDP	SRP	PP	DOP	TSS
		mg/L	mg/L	mg/L	mg/L	mg/L	mg/L		mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
	5/19 23:57	0.52	0.08	0.01	0.44	0.07		5/20 12:15	0.14	0.06	0.04	0.07	0.02	
	5/20 0:17	0.20	0.08	0.02	0.13	0.05		5/20 12:35	0.11	0.08	0.05	0.03	0.03	
	5/20 0:37	0.20	0.08	0.02	0.13	0.05		5/20 12:55	0.10	0.08	0.06	0.03	0.02	
	5/20 0:57	0.18	0.09	0.04	0.09	0.05		5/20 13:15	0.12	0.09	0.06	0.03	0.02	
								5/20 13:35	0.11	0.08	0.06	0.03	0.02	
								5/20 14:15	0.12	0.08	0.06	0.03	0.02	
								5/20 14:55	0.11	0.08	0.06	0.03	0.02	
								5/20 15:35	0.11	0.09	0.06	0.03	0.02	
								5/20 16:35	0.12	0.09	0.06	0.03	0.02	
								5/20 17:35	0.11	0.09	0.07	0.03	0.02	
								5/20 18:35	0.12	0.09	0.07	0.03	0.02	
	5/28 20:55	1.05	0.89	0.06	0.16	0.83								
	5/28 21:15	0.21		0.06										
	5/28 21:35	0.16	0.08	0.03	0.08	0.04								
	5/28 21:55	0.12		0.03										
	5/28 22:15	0.12	0.08	0.03	0.04	0.05								
	5/28 22:35	0.11	0.08	0.03	0.03	0.05								
	5/28 23:15	0.12	0.08	0.04	0.04	0.04								

	In							Out						
	Time	TP	TDP	SRP	PP	DOP	TSS	Time	TP	TDP	SRP	PP	DOP	TSS
		mg/L	mg/L	mg/L	mg/L	mg/L	mg/L		mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
								6/1 17:33	0.19	0.10	0.03	0.08	0.08	
								6/1 18:13	0.18	0.12	0.04	0.05	0.09	
								6/1 18:53	0.22	0.14	0.06	0.07	0.08	
								6/1 19:53	0.22	0.15	0.07	0.07	0.08	
								6/1 21:13	0.20	0.14	0.06	0.06	0.08	
								6/1 23:13	0.19	0.14	0.07	0.05	0.07	
	7/13 7:21	0.54	0.18	0.13	0.36	0.05	323.2	7/13 7:53	0.21	0.10	0.05	0.11	0.05	20.8
	7/13 7:41	0.19	0.10	0.07	0.09	0.04	40.8	7/13 8:33	0.14	0.07	0.04	0.07	0.03	1.2
								7/13 8:53	0.14	0.07	0.04	0.07	0.03	3.6
								7/13 9:13	0.22	0.08	0.04	0.14	0.04	4.4
								7/13 9:33	0.16	0.10	0.05	0.07	0.04	2.2

	In							Out						
	Time	TP	TDP	SRP	PP	DOP	TSS	Time	TP	TDP	SRP	PP	DOP	TSS
		mg/L	mg/L	mg/L	mg/L	mg/L	mg/L		mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
	7/17 16:43	0.90	0.05		0.85		567.6	7/17 17:17	0.16	0.04	0.02	0.12	0.02	46.4
	7/17 17:03	0.18	0.04	0.01	0.14	0.02	133.8	7/17 17:37	0.13	0.10	0.04	0.02	0.06	24.9
	7/17 17:23	0.16	0.04	0.02	0.11	0.03	90.5	7/17 17:57	0.09	0.08	0.03	0.01	0.04	13.4
	7/17 17:43	0.12	0.06	0.02	0.07	0.03	50.3	7/17 18:17	0.09	0.07	0.04	0.02	0.03	12.0
	7/17 18:03	0.16	0.06	0.02	0.09	0.04	63.9	7/17 18:37	0.12	0.09	0.04	0.02	0.05	14.7
								7/17 19:17	0.11	0.10	0.04	0.01	0.06	12.1
								7/17 19:57	0.11	0.10	0.05	0.00	0.06	12.9
								7/17 20:37	0.12	0.11	0.04	0.01	0.07	19.6
								7/17 21:37	0.10	0.09	0.05	0.01	0.05	13.4
								7/17 22:37	0.10	0.09	0.05	0.01	0.04	10.9
								7/17 23:37	0.12	0.10	0.05	0.02	0.05	3.2
								7/18 1:17	0.20	0.11	0.06	0.09		5.7
	7/18 22:21	0.72	0.06	0.03	0.65	0.03		7/18 23:17	0.12	0.09	0.07	0.03	0.03	
	7/18 22:41	0.25	0.04	0.02	0.21	0.02		7/18 23:37	0.13	0.09	0.07	0.04	0.03	
	7/18 23:01	0.48	0.04	0.02	0.44	0.02		7/18 23:57	0.12	0.09	0.07	0.02	0.03	
	7/18 23:21	0.10	0.03	0.02	0.06	0.01		7/19 0:37	0.09	0.07	0.04	0.02	0.04	
	7/18 23:41	0.09	0.04	0.02	0.05	0.02		7/19 1:17	0.10	0.07	0.05	0.03	0.02	
	7/19 0:01	0.11	0.05	0.03	0.06	0.02		7/19 1:57	0.14	0.10	0.06	0.04	0.04	
	7/19 0:21	0.09	0.05	0.03	0.04	0.03		7/19 2:57	0.12	0.07	0.06	0.05	0.02	
	7/19 0:41	0.12	0.03	0.02	0.09	0.01		7/19 3:57	0.10	0.07	0.05	0.03	0.02	
	7/19 1:41	0.17	0.05	0.02	0.12	0.02		7/19 4:57	0.10	0.08	0.05	0.02	0.02	
	7/19 2:21	0.28	0.05	0.03	0.23	0.02		7/19 6:37	0.11	0.08	0.06	0.04	0.02	

	In							Out						
	Time	TP	TDP	SRP	PP	DOP	TSS	Time	TP	TDP	SRP	PP	DOP	TSS
		mg/L	mg/L	mg/L	mg/L	mg/L	mg/L		mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
	8/9 5:51	0.66	0.06	0.02	0.61	0.04	342.0	8/9 8:57	0.10	0.07	0.04	0.03	0.03	17.6
	8/9 6:11	0.26	0.10	0.06	0.16	0.04	100.3	8/9 9:17	0.08	0.07	0.04	0.02	0.03	16.3
	8/9 6:31	0.25	0.12	0.11	0.13	0.01	118.1	8/9 9:37	0.10	0.07	0.04	0.03	0.03	5.9
	8/9 6:51	0.15	0.09	0.07	0.06	0.02	55.7	8/9 9:57	0.08	0.06	0.03	0.02	0.03	4.4
	8/9 7:11	0.15	0.09	0.07	0.06	0.02	66.2	8/9 10:17	0.09	0.04	0.02	0.05	0.02	4.6
	8/9 7:31	0.17	0.08	0.06	0.09	0.02	88.9	8/9 10:57	0.10	0.07	0.05	0.03	0.03	3.5
	8/9 7:51	0.21	0.08	0.05	0.14	0.02	154.3	8/9 11:37	0.10	0.06	0.04	0.04	0.02	4.0
	8/9 8:11	0.20	0.09	0.05	0.11	0.04	104.5	8/9 12:17	0.09	0.08	0.04	0.01	0.04	2.4
	8/9 8:31	0.31	0.07	0.05	0.24	0.02	273.2	8/9 13:17	0.12	0.06	0.04	0.06	0.02	2.1
	8/9 9:31	0.22	0.13	0.09	0.10	0.03	190.9	8/9 14:17	0.10	0.07	0.05	0.03	0.02	0.5
	8/9 10:31	0.12	0.06	0.04	0.06	0.03	60.8	8/9 15:17	0.10	0.07	0.05	0.03	0.02	1.9
								8/9 16:57	0.10	0.07	0.05	0.03	0.02	0.5

	In							Out						
	Time	TP	TDP	SRP	PP	DOP	TSS	Time	TP	TDP	SRP	PP	DOP	TSS
		mg/L	mg/L	mg/L	mg/L	mg/L	mg/L		mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
	11/12 1:29	0.75	0.31	0.24	0.44	0.06	304.9	11/12 7:15	0.11	0.05	0.03	0.06	0.02	31.1
	11/12 1:49	0.28	0.11	0.08	0.17	0.03	228.4	11/12 7:35	0.08	0.04	0.03	0.03	0.02	7.2
	11/12 2:09	0.17	0.10	0.05	0.07	0.05	99.2	11/12 8:15	0.03	0.03	0.02	0.00	0.01	10.9
	11/12 2:29	0.11	0.06	0.05	0.05	0.02	47.4	11/12 8:35	0.07	0.03	0.02	0.04	0.01	14.0
	11/12 2:49	0.09	0.06	0.04	0.03	0.02	31.6	11/12 9:15	0.04	0.03	0.02	0.01	0.01	7.5
	11/12 3:09	0.09	0.06	0.04	0.03	0.02	24.1	11/12 9:55	0.06	0.03	0.02	0.03	0.01	9.1
	11/12 3:29	0.10	0.07	0.05	0.04	0.02	16.3	11/12 11:35	0.04	0.03	0.02	0.01	0.01	6.8
	11/12 3:49	0.11	0.08	0.06	0.03	0.02	23.8	11/12 12:35	0.04	0.03	0.02	0.01	0.01	0.6
	11/12 6:09	0.10	0.06	0.04	0.04	0.02	40.8	11/12 13:35	0.05	0.03	0.02	0.02	0.01	4.5
	11/12 7:29	0.12	0.04	0.03	0.08	0.02	39.7	11/12 15:15	0.04	0.04	0.02	0.00	0.01	1.0
2013	1/29 21:11	1.58	0.06	0.02	1.51	0.04	1273.8	1/29 21:48	0.25	0.03	0.01	0.21	0.02	99.3
	1/29 21:31	0.43	0.05	0.02	0.38	0.03	237.3	1/29 22:08	0.15	0.03	0.01	0.12	0.02	29.8
	1/29 21:51	0.16	0.06	0.02	0.10	0.04	35.1	1/29 22:28	0.08	0.03	0.01	0.04	0.02	9.6
	1/29 22:11	0.19	0.06	0.02	0.14	0.04	72.2	1/29 22:48	0.08	0.04	0.01	0.03	0.03	18.3
	1/29 22:31	0.20	0.04	0.01	0.15	0.03	221.3	1/29 23:08	0.10	0.04	0.01	0.06	0.03	43.4
	1/29 22:51	0.23	0.05	0.01	0.18	0.03	122.5	1/29 23:48	0.10	0.04	0.01	0.06	0.03	30.7
	1/29 23:11	0.17	0.04	0.01	0.12	0.03	80.2	1/30 0:28	0.10	0.04	0.01	0.06	0.03	36.4
	1/29 23:31	0.15	0.05	0.01	0.10	0.03	71.8	1/30 2:08	0.13	0.08	0.02	0.05	0.06	35.7
	1/29 23:51	0.19	0.06	0.02	0.13	0.04	52.2	1/30 3:08	0.18	0.06	0.02	0.12	0.04	66.3
	1/30 1:51	0.16	0.06	0.02	0.10	0.04	40.9	1/30 4:08	0.09	0.04	0.01	0.05	0.03	17.0
	1/30 3:11		0.06	0.02		0.04	12.4	1/30 5:48	0.06	0.04	0.01	0.02	0.03	0.5

	In							Out						
	Time	TP	TDP	SRP	PP	DOP	TSS	Time	TP	TDP	SRP	PP	DOP	TSS
		mg/L	mg/L	mg/L	mg/L	mg/L	mg/L		mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
	2/12 18:27	0.53	0.04	0.02	0.49	0.02		2/12 20:02	0.16	0.07	0.04	0.09	0.03	
	2/12 19:07	0.28	0.05	0.02	0.24	0.02		2/12 20:22	0.14	0.05	0.03	0.08	0.02	
	2/12 19:47	0.27	0.05	0.04	0.22	0.01		2/12 20:42	0.09	0.05	0.04	0.04	0.01	
								2/12 21:22	0.09	0.04	0.03	0.04	0.01	
								2/12 22:02	0.09	0.04	0.03	0.05	0.02	
								2/12 23:22	0.07	0.05	0.03	0.02	0.02	
								2/13 0:22	0.07	0.05	0.03	0.01	0.03	
								2/13 1:22	0.06	0.05	0.03	0.01	0.02	
								2/13 2:22	0.06	0.05	0.03	0.01	0.02	
								2/13 4:02	0.09	0.07	0.03	0.02	0.04	

	In							Out						
	Time	TP	TDP	SRP	PP	DOP	TSS	Time	TP	TDP	SRP	PP	DOP	TSS
		mg/L	mg/L	mg/L	mg/L	mg/L	mg/L		mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
	2/25 19:31	0.27	0.02	0.01	0.24	0.02	194.4	2/25 21:01	0.14	0.07	0.02	0.07	0.05	13.30
	2/25 19:51	0.19	0.03	0.01	0.16	0.02	95.0	2/25 21:21	0.09	0.03	0.01	0.06	0.02	20.60
	2/25 20:51	0.14	0.05	0.01	0.10	0.03	70.0	2/25 21:41	0.17	0.06	0.02	0.11	0.04	56.00
	2/25 21:11	0.14	0.02	0.01	0.12	0.01	66.7	2/25 22:01	0.10	0.07	0.02	0.03	0.05	7.60
	2/25 21:31	0.16	0.05	0.01	0.12	0.03	85.7	2/25 22:21	0.16	0.03	0.01	0.13	0.02	52.90
	2/25 21:51	0.09	0.02	0.01	0.07	0.01	50.8	2/25 23:01	0.07	0.07	0.02	0.00	0.05	8.90
	2/25 22:11	0.19	0.03	0.01	0.16	0.02	92.0	2/25 23:41	0.09	0.07	0.02	0.03	0.05	5.10
	2/25 23:11	0.09	0.03	0.01	0.07	0.02	35.4	2/26 0:21	0.27	0.07	0.02	0.20	0.05	12.50
								2/26 1:21	0.08	0.08	0.02	0.01	0.06	3.20
								2/26 2:21	0.08	0.08	0.02	0.01	0.06	17.60
								2/26 3:21	0.09	0.08	0.02	0.01	0.06	17.70
								2/26 5:01	0.10	0.10	0.03	0.00	0.07	5.80
	3/11 7:01	0.26	0.04	0.01	0.22	0.03	187.7	3/11 11:45	0.13	0.06	0.05	0.07	0.01	12.90
	3/11 7:41	0.31	0.03	0.02	0.28	0.01	248.8	3/11 12:45	0.13	0.07	0.06	0.05	0.01	10.80
	3/11 8:01	0.22	0.03	0.02	0.18	0.01	143.4							
	3/11 10:41	0.17	0.03	0.01	0.14	0.02								
	3/11 11:41						75.5							

2. Event Based Summary for P species and TSS.

Time	TSS in	TSS out	TP in	TP out	TDP in	TDP out	DRP in	DRP out	PP in	PP out	DOP in	DOP out
	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
1-Aug-11	298	9.89	0.40	0.16	0.03	0.08			0.37	0.08		
6-Aug-11	141	7.16	0.16	0.11	0.03	0.08			0.13	0.03		
13-Aug-11	81	4.69	0.19	0.14	0.05	0.11			0.14	0.04		
27-Aug-11	33	1.22	0.16	0.11	0.12	0.07			0.05	0.04		
2-Sep-11	32		0.34	N/A	0.16	N/A			0.18			
3-Sep-11	29		0.14		0.07				0.07			
5-Sep-11		1.03		0.08		0.07				0.01		
15-Sep-11	117	0.00	0.37	0.00	0.16	0.00			0.21	0.00		0.00
23-Sep-11	90	2.68	0.19	0.10	0.04	0.08			0.14	0.02		
26-Oct-11	166		0.30		0.11		0.07		0.20		0.04	
10-Nov-11	123	0.00	0.50	0.00	0.19	0.00	0.13	0.00	0.31	0.00	0.06	0.00
16-Nov-11	24		0.53		0.35		0.28		0.18		0.07	
1-Feb-12	127	0.00	0.28	0.00	0.03	0.00		0.00	0.25	0.00		0.00
8-Feb-12	104	0.00	0.27	0.00	0.05	0.00	0.02	0.00	0.23	0.00	0.02	0.00
2-Mar-12	71	1.62	0.27	0.09	0.03	0.07	0.02	0.05	0.23	0.02	0.02	0.01
28-Apr-12	95	0.00	0.37	0.00	0.10	0.00	0.04	0.00	0.27	0.00	0.06	0.00
1-May-12	223	0.00	0.32	0.00	0.04	0.00	0.01	0.00	0.27	0.00	0.03	0.00
8-May-12	78	0.00	0.48	0.00	0.21	0.00	0.13	0.00	0.27	0.00	0.08	0.00
9-May-12	230		0.32		0.03		0.01		0.29		0.02	
20-May-12			0.25	0.11	0.08	0.09	0.03	0.06	0.17	0.03	0.06	0.02

Time	TSS in	TSS out	TP in	TP out	TDP in	TDP out	DRP in	DRP out	PP in	PP out	DOP in	DOP out
	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
29-May-12			0.81		0.66		0.05		0.14		0.61	
14-Jul-12	225	3.07	0.42	0.17	0.15	0.09	0.11	0.05	0.27	0.08	0.04	0.04
18-Jul-12	249	15.61	0.39	0.12	0.05	0.09	0.01	0.04	0.34	0.03	0.03	0.05
19-Jul-12			0.35	0.12	0.04	0.08	0.02	0.06	0.30	0.03	0.02	0.03
10-Aug-12	200	6.20	0.29	0.10	0.10	0.06	0.07	0.04	0.19	0.03	0.02	0.03
13-Nov-12	110	5.34	0.22	0.05	0.10	0.03	0.06	0.02	0.12	0.02	0.03	0.01
30-Jan-13	189	33.35	0.33	0.12	0.06	0.05	0.02	0.02	0.27	0.06	0.04	0.04
13-Feb-13			0.31	0.08	0.05	0.05	0.03	0.03	0.27	0.03	0.02	0.02
26-Feb-13	62	11.46	0.13	0.11	0.03	0.07	0.01	0.02	0.10	0.05	0.02	0.05
11-Mar-13	94	11.94	0.19	0.13	0.03	0.06	0.01	0.05	0.16	0.06	0.02	0.01
12-Apr-13			0.61	0.14	0.26	0.10	0.22	0.07	0.34	0.05	0.04	0.03

Appendix 3: Media Data for Enhanced P Removal Bioretention Site

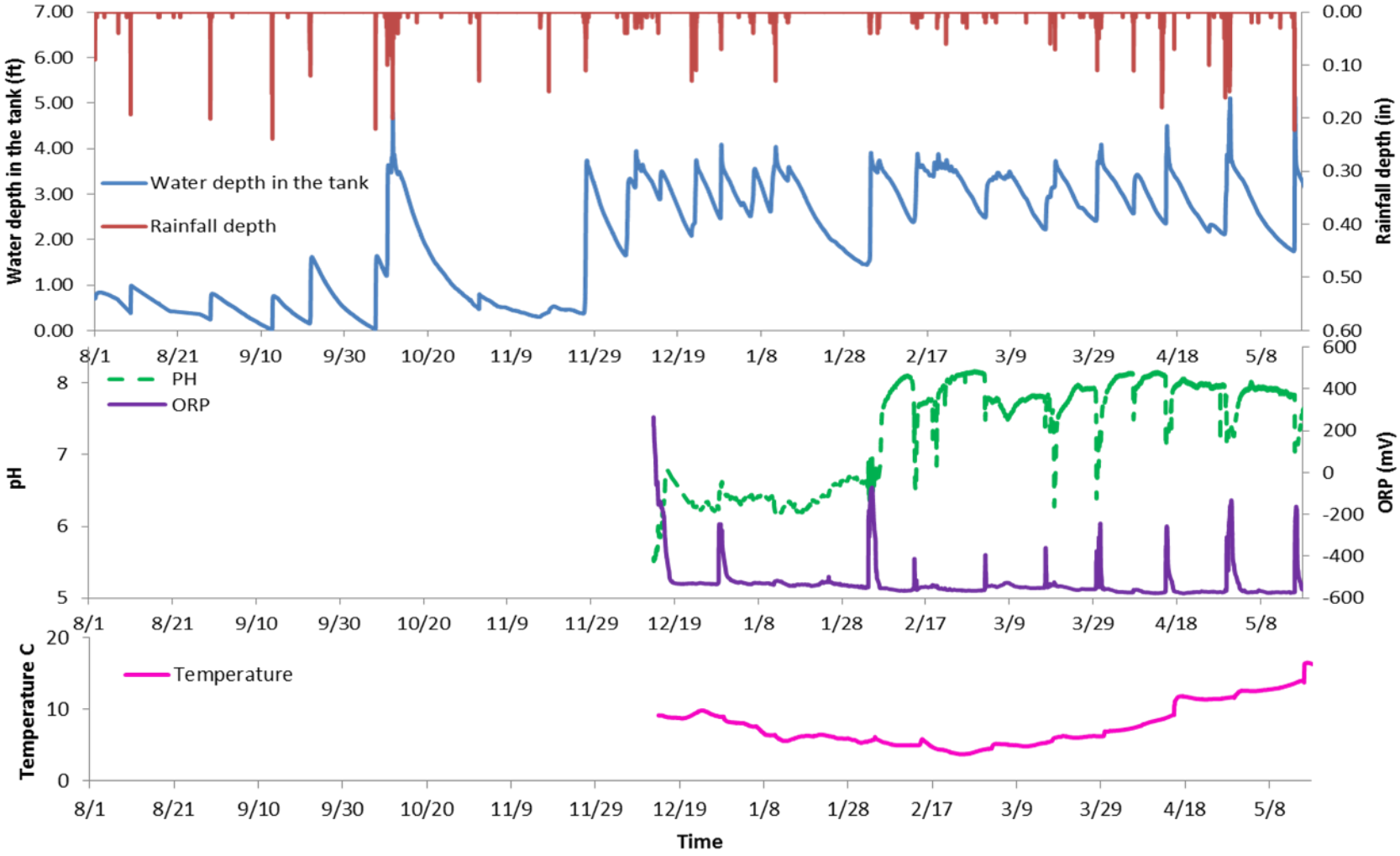
26-Apr-11						31-Aug-11				
Pox	mg P / kg soil					Pox	mg P / kg soil			
Layer	Group 1	Group 2	Group 3	Group 4		Layer	Group 1	Group 2	Group 3	Group 4
0-2	294.12	232.48	221.38	108.45		0-2	47.43	40.95	44.20	17.98
2-4	141.06	215.39	118.60	79.43		2-4	36.48	47.38	44.10	20.13
4-8	22.27	102.76	40.47	48.33		4-8	127.01	139.85	60.56	58.14
8-12	19.27	38.69	50.27	58.16		8-12	399.00	419.41	94.20	84.22
12-24	27.13	34.91	52.39	53.33		12-24	66.14	118.22	57.25	101.80
Alox	mg Al / kg soil					Alox	mg Al / kg soil			
Layer	Group 1	Group 2	Group 3	Group 4		Layer	Group 1	Group 2	Group 3	Group 4
0-2	1151.07	870.57	801.99	764.31		0-2	217.31	234.15	175.51	159.73
2-4	571.96	629.98	251.25	305.44		2-4	168.53	245.12	324.27	205.93
4-8	40.06	39.90	39.75	40.06		4-8	2507.13	1715.14	524.58	422.62
8-12	39.90	39.91	39.86	40.03		8-12	8746.01	7996.81	4494.82	441.82
12-24	40.04	40.02	39.99	39.88		12-24	997.50	1132.84	3894.29	333.13
Feox	mg Fe / kg soil					Feox	mg Fe / kg soil			
Layer	Group 1	Group 2	Group 3	Group 4		Layer	Group 1	Group 2	Group 3	Group 4
0-2	4618.71	4834.52	3853.11	2043.00		0-2	880.93	951.63	840.64	793.46
2-4	2456.72	4603.72	2586.92	1880.39		2-4	737.65	994.20	900.63	785.67
4-8	535.20	1970.37	857.79	1174.71		4-8	1309.40	1509.39	1070.39	1120.37
8-12	455.71	648.15	1160.60	1112.89		8-12	2271.65	3004.95	1838.41	1414.43
12-24	562.91	757.22	908.51	889.55		12-24	925.87	1353.34	1079.96	1305.75

9-Mar-12						16-Oct-12				
Pox	mg P / kg soil					Pox	mg P / kg soil			
Layer	Group 1	Group 2	Group 3	Group 4		Layer	Group 1	Group 2	Group 3	Group 4
0-2	125.17	224.92	85.63	107.90		0-2	91.69	112.81	194.51	79.74
2-4	120.30	244.73	111.53	109.63		2-4	95.23	189.66	104.30	87.92
4-8	101.76	198.82	85.75	74.47		4-8	116.48	141.21	144.59	86.97
8-12	104.36	106.98	70.19	86.13		8-12	132.74	185.18	120.11	104.57
12-24	67.32	81.95	63.10	71.87		12-24	79.73	191.95	106.40	121.89
Alox	mg Al / kg soil					Alox	mg Al / kg soil			
Layer	Group 1	Group 2	Group 3	Group 4		Layer	Group 1	Group 2	Group 3	Group 4
0-2	3107.57	4519.93	2377.03	2071.68		0-2	1433.64	2565.36	2766.44	910.91
2-4	2877.28	5446.40	2712.68	2465.37		2-4	1688.47	3347.29	1846.93	1325.24
4-8	2473.58	4108.60	2292.65	1652.04		4-8	1805.48	2562.46	2129.31	1123.40
8-12	2812.62	2481.77	2123.96	1599.68		8-12	2123.63	2860.92	1582.05	1434.70
12-24	1367.66	1466.15	1107.68	1081.19		12-24	1191.63	2613.59	1274.01	1146.73
Feox	mg Fe / kg soil					Feox	mg Fe / kg soil			
Layer	Group 1	Group 2	Group 3	Group 4		Layer	Group 1	Group 2	Group 3	Group 4
0-2	1505.98	2444.92	1152.03	864.60		0-2	806.24	1404.52	1921.22	792.08
2-4	1548.08	3421.64	1370.90	950.02		2-4	1071.88	1413.74	1309.00	1023.37
4-8	1118.75	2141.67	917.13	907.82		4-8	885.42	1678.19	1421.50	874.03
8-12	1033.56	1684.88	903.08	713.63		8-12	1132.71	1816.18	1230.86	1091.60
12-24	1125.53	1252.05	922.77	789.95		12-24	1036.18	1722.58	1117.20	841.56

1-Mar-13				
Pox	mg P / kg soil			
Layer	Group 1	Group 2	Group 3	Group 4
0-2	99.71	174.05	84.65	78.64
2-4	101.21	148.19	100.49	86.65
4-8	66.43	300.77	112.82	103.55
8-12	133.92	403.21	131.08	82.21
12-24	38.04	212.24	79.98	62.87
Alox	mg Al / kg soil			
Layer	Group 1	Group 2	Group 3	Group 4
0-2	1911.06	2899.85	1581.14	1116.74
2-4	2013.30	2183.31	1606.48	1431.61
4-8	1302.68	4314.26	2029.61	1752.59
8-12	1980.70	7690.80	1932.25	1249.83
12-24	603.10	3165.97	1324.04	1136.48
Feox	mg Fe / kg soil			
Layer	Group 1	Group 2	Group 3	Group 4
0-2	1286.53	2729.83	1010.67	716.10
2-4	1535.15	2052.59	886.61	898.26
4-8	1051.72	4305.91	1555.42	1351.73
8-12	1155.44	3938.03	1931.82	976.17
12-24	399.41	2554.72	867.54	516.54

Appendix 4: Hydrological and Water Quality Data for Enhanced N Removal Site

1. Onsite Monitoring Data in the Denitrification Vault (ORP is reffered to the Ag/AgCl electrode).



2. Water Quality Data of the Porous Pavement Effluent (EMCs).

Time	Rainfall depth	TN	DN	NO_3^-	NO_2^-	NH_4^+	PON	DON	TON	N_{ox}
	cm	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
21-Sep-13	2.46	2.13	1.87	1.32	0.04	0.11	0.25	0.40	0.66	1.36
7-Oct-13	2.49	1.42	1.19	0.72	0.03	0.05	0.23	0.40	0.63	0.74
10-Oct-13	10.01	0.65	0.60	0.44	0.02	0.05	0.06	0.09	0.15	0.46
1-Nov-13	0.56	1.47	0.39	0.26	0.00	0.05	1.09	0.07	1.16	0.26
16-Nov-13	0.84	1.58	1.05	0.34	0.06	0.05	0.52	0.60	1.12	0.41
18-Nov-13	0.43	0.81	0.32	0.20	0.01	0.05	0.49	0.07	0.56	0.21
26-Nov-13	5.46	0.56	0.44	0.18	0.01	0.07	0.12	0.18	0.30	0.19
6-Dec-13	2.31	0.48	0.44	0.31	0.02	0.05	0.04	0.07	0.11	0.32
9-Dec-13	3.02	0.38	0.35	0.23	0.01	0.10	0.03	0.01	0.04	0.24
3-Feb-14	3.35	0.98	0.75	0.35	0.02	0.11	0.23	0.27	0.50	0.37
5-Feb-14	1.07	0.71	0.59	0.35	0.02	0.09	0.12	0.13	0.25	0.37
19-Feb-14	0.33	1.72	0.56	0.30	0.01	0.08	1.16	0.18	1.34	0.31
21-Feb-14	0.38	0.72	0.66	0.39	0.01	0.05	0.06	0.20	0.27	0.40
3-Mar-14	1.07	0.98	0.94	0.64	0.02	0.10	0.04	0.18	0.23	0.66
17-Mar-14	0.58	0.99	0.77	0.68	0.01	0.05	0.22	0.03	0.25	0.69
19-Mar-14	1.04	0.64	0.60	0.48	0.01	0.06	0.03	0.06	0.09	0.49
29-Mar-14	5.18	0.33	0.31	0.26	0.01	0.05	0.02	0.00	0.02	0.26
7-Apr-14	1.60	0.76	0.73	0.58	0.01	0.07	0.04	0.07	0.11	0.59
15-Apr-14	5.89	0.76	0.57	0.50	0.01	0.05	0.19	0.01	0.20	0.51
20-Apr-14	0.08	0.65	0.60	0.51	0.01	0.05	0.05	0.04	0.09	0.52
29-Apr-14	10.21	1.02	0.99	0.76	0.01	0.05	0.03	0.17	0.20	0.77

3. Water Quality Data of the Denitrification Vault.

Time	TN	DN	NO_3^-	NO_2^-	NH_4^+	PON	DON	TON	N_{ox}
	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
9/22/2013 11:40	1.15	0.95	0.46	0.025	0.19	0.20	0.27	0.48	0.48
9/22/2013 17:40	0.95	0.79	0.47	0.027	0.14	0.16	0.14	0.31	0.50
9/22/2013 23:40	0.96	0.72	0.37	0.038	0.05	0.24	0.26	0.50	0.41
9/23/2013 5:40	0.88	0.68	0.41	0.040	0.09	0.20	0.14	0.34	0.45
9/23/2013 11:40	0.91	0.74	0.38	0.036	0.05	0.17	0.27	0.44	0.42
9/24/2013 12:30	0.78	0.57	0.24	0.019	0.05	0.21	0.26	0.47	0.26
9/25/2013 11:00	0.75	0.58	0.19	0.016	0.05	0.17	0.32	0.49	0.21
9/26/2013 11:30	0.60	0.56	0.18	0.011	0.05	0.04	0.32	0.36	0.19
9/27/2013 10:30	0.61	0.46	0.13	0.008	0.05	0.15	0.27	0.42	0.14
9/30/2013 10:30	0.58	0.44	0.11	0.006	0.05	0.14	0.28	0.42	0.11
10/1/2013 12:30	0.70	0.50	0.09	0.005	0.15	0.20	0.26	0.46	0.10
10/2/2013 14:20	0.66	0.40	0.11	0.005	0.05	0.27	0.23	0.50	0.11
10/7/2013 12:16	1.11	0.82	0.21	0.010	0.11	0.29	0.49	0.79	0.22
10/7/2013 12:56	0.91	0.85	0.27	0.018	0.19	0.06	0.37	0.43	0.29
10/7/2013 13:36	0.88	0.79	0.32	0.017	0.23	0.09	0.23	0.31	0.34
10/7/2013 14:36	0.90	0.76	0.33	0.022	0.13	0.14	0.28	0.42	0.35
10/7/2013 15:36	0.90	0.77	0.34	0.041	0.14	0.13	0.25	0.38	0.38
10/7/2013 17:36	0.83	0.70	0.33	0.023	0.14	0.13	0.22	0.34	0.35
10/7/2013 19:36	0.77	0.65	0.33	0.022	0.11	0.13	0.18	0.31	0.36

Time	TN	DN	NO_3^-	NO_2^-	NH_4^+	PON	DON	TON	N_{ox}
	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
10/8/2013 1:36	0.87	0.71	0.32	0.021	0.16	0.16	0.21	0.37	0.34
10/8/2013 7:36	0.83	0.66	0.33	0.021	0.14	0.17	0.17	0.34	0.35
10/8/2013 12:20	0.78	0.59	0.31	0.020	0.05	0.19	0.21	0.40	0.33
10/9/2013 12:20	0.62	0.57	0.26	0.012	0.05	0.06	0.25	0.30	0.27
10/10/2013 5:28	0.62	0.47	0.22	0.005	0.05	0.14	0.20	0.35	0.22
10/10/2013 11:28	0.61	0.55	0.27	0.009	0.05	0.06	0.22	0.28	0.28
10/10/2013 16:45	0.62	0.53	0.31	0.008	0.05	0.09	0.16	0.25	0.32
10/10/2013 22:45	0.55	0.36	0.29	0.014	0.05	0.20	0.00	0.20	0.30
10/11/2013 4:45	0.55	0.37	0.28	0.010	0.05	0.18	0.04	0.21	0.29
10/11/2013 8:30	0.55	0.38	0.25	0.011	0.05	0.17	0.07	0.24	0.26
11/4/2013 10:40	0.57	0.51	0.21	0.004	0.05	0.06	0.25	0.31	0.21
11/5/2013 13:30	0.56	0.31	0.15	0.002	0.05	0.25	0.10	0.36	0.16
11/11/2013 10:15	0.49	0.22	0.15	0.002	0.05	0.27	0.02	0.29	0.15
11/13/2013 11:00	0.50	0.42	0.08	0.002	0.05	0.07	0.29	0.37	0.08
11/14/2013 12:00	0.47	0.47	0.17	0.000	0.05	0.00	0.25	0.25	0.17
11/16/2013 6:05	0.51	0.40	0.09	0.003	0.05	0.11	0.26	0.37	0.09
11/16/2013 12:05	0.68	0.60	0.12	0.027	0.05	0.08	0.40	0.48	0.15
11/18/2013 12:05	0.51	0.46	0.08	0.003	0.05	0.05	0.32	0.38	0.08
11/19/2013 0:05	0.55	0.41	0.07	0.003	0.05	0.14	0.29	0.43	0.07
11/19/2013 10:30	0.52	0.46	0.09	0.003	0.05	0.06	0.32	0.38	0.09

Time	TN	DN	NO_3^-	NO_2^-	NH_4^+	PON	DON	TON	N_{ox}
	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
11/20/2013 10:40	0.46	0.45	0.15	0.003	0.05	0.01	0.25	0.26	0.15
11/21/2013 12:40	0.57	0.43	0.13	0.003	0.05	0.15	0.24	0.39	0.13
11/22/2013 14:50	0.62	0.43	0.13	0.003	0.05	0.20	0.24	0.44	0.13
11/25/2013 0:20	0.50	0.27	0.10	0.003	0.05	0.23	0.12	0.35	0.10
11/26/2013 14:27	0.54	0.23	0.15	0.005	0.05	0.31	0.03	0.34	0.15
11/26/2013 15:07	0.87	0.84	0.11	0.004	0.13	0.02	0.59	0.62	0.11
11/26/2013 15:47	0.53	0.48	0.12	0.007	0.05	0.05	0.30	0.35	0.13
11/26/2013 16:47	0.41	0.24	0.12	0.005	0.05	0.17	0.06	0.23	0.13
11/26/2013 17:47	0.36	0.25	0.09	0.010	0.05	0.11	0.10	0.20	0.10
11/26/2013 19:47	0.51	0.23	0.16	0.009	0.05	0.28	0.01	0.29	0.17
11/26/2013 21:47	0.67	0.32	0.17	0.020	0.12	0.35	0.01	0.36	0.19
11/27/2013 3:47	0.59	0.33	0.18	0.012	0.11	0.26	0.03	0.30	0.19
11/27/2013 9:47	0.50	0.33	0.21	0.019	0.10	0.17	0.00	0.17	0.23
11/27/2013 15:37	0.65	0.65	0.28	0.014	0.14	0.00	0.23	0.22	0.29
11/28/2013 3:37	0.60	0.58	0.16	0.014	0.05	0.03	0.35	0.37	0.17
11/28/2013 15:37	0.61	0.45	0.13	0.014	0.05	0.16	0.26	0.42	0.14
11/29/2013 3:37	0.58	0.47	0.12	0.014	0.05	0.10	0.29	0.39	0.14
11/29/2013 15:37	0.61	0.40	0.11	0.015	0.05	0.22	0.22	0.44	0.13
11/30/2013 15:37	0.70	0.43	0.12	0.008	0.05	0.28	0.25	0.53	0.13
12/1/2013 13:30	0.54	0.42	0.14	0.017	0.05	0.12	0.21	0.33	0.16
12/2/2013 10:00	0.60	0.41	0.12	0.100	0.10	0.19	0.08	0.28	0.22

Time	TN	DN	NO_3^-	NO_2^-	NH_4^+	PON	DON	TON	N_{ox}
	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
12/7/2013 0:09	0.27	0.27	0.13	0.006	0.09	0.00	0.05	0.05	0.13
12/7/2013 0:49	0.30	0.27	0.14	0.004	0.05	0.02	0.08	0.11	0.14
12/7/2013 1:29	0.26	0.23	0.16	0.006	0.05	0.03	0.02	0.05	0.16
12/7/2013 2:29	0.31	0.20	0.14	0.007	0.05	0.11	0.00	0.11	0.15
12/7/2013 3:29	0.26	0.22	0.15	0.005	0.05	0.04	0.02	0.05	0.15
12/7/2013 5:29	0.28	0.19	0.12	0.007	0.05	0.09	0.02	0.11	0.12
12/7/2013 7:29	0.29	0.29	0.09	0.008	0.05	0.00	0.15	0.14	0.09
12/7/2013 13:29	0.28	0.21	0.07	0.006	0.05	0.07	0.08	0.15	0.08
12/7/2013 19:29	0.26	0.21	0.13	0.006	0.05	0.05	0.03	0.08	0.13
12/9/2013 11:30	0.36	0.22	0.11	0.005	0.05	0.14	0.05	0.19	0.12
12/11/2013 16:30	0.37	0.25	0.18	0.004	0.05	0.12	0.01	0.13	0.18
12/13/2013 11:10	0.58	0.54	0.27	0.002	0.05	0.04	0.22	0.26	0.27
12/15/2013 6:50	0.46	0.40	0.11	0.005	0.05	0.06	0.24	0.30	0.12
12/15/2013 18:50	0.44	0.37	0.12	0.004	0.05	0.07	0.19	0.26	0.12
12/16/2013 6:50	0.45	0.40	0.07	0.003	0.05	0.05	0.28	0.33	0.07
12/16/2013 11:20	0.43	0.39	0.11	0.003	0.05	0.04	0.22	0.26	0.12
12/17/2013 13:00	0.42	0.37	0.16	0.003	0.05	0.05	0.17	0.22	0.16
1/28/2014 11:30	0.45	0.45	0.07	0.005	0.04	0.00	0.33	0.33	0.07
1/29/2014 15:00	0.62	0.27	0.05	0.005	0.14	0.34	0.08	0.42	0.06
2/4/2014 16:00	1.11	1.01	0.28	0.049	0.20	0.10	0.49	0.59	0.33

Time	TN	DN	NO_3^-	NO_2^-	NH_4^+	PON	DON	TON	N_{ox}
	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
2/5/2014 5:54	1.00	0.88	0.28	0.050	0.20	0.12	0.36	0.48	0.33
2/5/2014 11:20	1.03	0.84	0.26	0.049	0.17	0.19	0.36	0.55	0.31
2/5/2014 15:20	0.99	0.84	0.28	0.047	0.20	0.15	0.31	0.46	0.33
2/5/2014 19:20	0.98	0.83	0.28	0.043	0.15	0.15	0.36	0.51	0.32
2/5/2014 23:20	1.03	0.81	0.26	0.044	0.13	0.21	0.38	0.59	0.31
2/6/2014 10:00	1.89	0.83	0.23	0.037	0.16	1.05	0.41	1.47	0.26
2/7/2014 14:10	0.85	0.46	0.31	0.019	0.10	0.38	0.04	0.42	0.33
2/10/2014 15:00	0.57	0.51	0.32	0.023	0.12	0.06	0.04	0.10	0.34
2/11/2014 15:00	0.53	0.46	0.20	0.032	0.09	0.07	0.15	0.21	0.23
2/12/2014 13:30	0.39	0.36	0.25	0.008	0.05	0.03	0.05	0.08	0.26
2/17/2014 15:40	0.37	0.29	0.22	0.011	0.05	0.08	0.01	0.09	0.23
2/18/2014 16:00	0.33	0.29	0.22	0.010	0.05	0.05	0.00	0.05	0.23
2/19/2014 10:30	0.65	0.54	0.28	0.014	0.05	0.11	0.20	0.31	0.29
2/19/2014 11:10	0.73	0.59	0.28	0.015	0.05	0.14	0.25	0.38	0.29
2/19/2014 11:50	0.75	0.65	0.29	0.014	0.09	0.09	0.27	0.36	0.30
2/19/2014 12:50	0.67	0.60	0.28	0.014	0.05	0.07	0.26	0.32	0.30
2/19/2014 13:50	0.66	0.55	0.28	0.015	0.05	0.10	0.21	0.31	0.29
2/19/2014 15:50	0.66	0.56	0.28	0.014	0.05	0.10	0.22	0.32	0.30
2/19/2014 17:50	0.72	0.56	0.28	0.014	0.05	0.16	0.22	0.38	0.29
2/19/2014 23:50	0.68	0.57	0.28	0.013	0.16	0.11	0.12	0.23	0.29
2/20/2014 10:00	0.75	0.55	0.27	0.012	0.05	0.20	0.21	0.42	0.28

Time	TN	DN	NO_3^-	NO_2^-	NH_4^+	PON	DON	TON	N_{ox}
	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
2/24/2014 13:30	0.60	0.59	0.37	0.011	0.05	0.01	0.16	0.17	0.38
2/25/2014 15:30	0.56	0.56	0.24	0.012	0.05	0.00	0.25	0.26	0.25
2/27/2014 11:00	0.71	0.55	0.05	0.01	0.09	0.16	0.40	0.56	0.06
2/28/2014 14:00	0.66	0.61	0.05	0.02	0.08	0.05	0.47	0.52	0.07
3/3/2014 18:00	0.62	0.57	0.05	0.02	0.19	0.04	0.31	0.35	0.07
3/4/2014 6:00	0.59	0.53	0.05	0.02	0.09	0.06	0.38	0.43	0.07
3/6/2014 16:20	0.83	0.51	0.05	0.03	0.20	0.32	0.23	0.55	0.08
3/7/2014 13:30	0.74	0.52	0.05	0.03	0.30	0.22	0.14	0.36	0.08
3/10/2014 13:50	0.60	0.39	0.05	0.02	0.24	0.21	0.09	0.29	0.07
3/12/2014 16:30	0.76	0.58	0.05	0.04	0.28	0.19	0.21	0.39	0.09
3/14/2014 12:30	0.75	0.47	0.05	0.04	0.23	0.28	0.15	0.43	0.09
3/15/2014 10:00	0.66	0.43	0.05	0.04	0.23	0.23	0.12	0.34	0.09
3/17/2014 5:10	0.69	0.47	0.05	0.02	0.24	0.22	0.16	0.39	0.07
3/17/2014 17:10	0.67	0.50	0.05	0.02	0.24	0.17	0.19	0.36	0.07
3/18/2014 5:10	0.68	0.58	0.13	0.03	0.20	0.10	0.23	0.32	0.15
3/18/2014 17:10	0.71	0.67	0.14	0.03	0.24	0.04	0.26	0.30	0.17
3/19/2014 5:10	0.69	0.65	0.21	0.02	0.15	0.04	0.27	0.31	0.23
3/19/2014 17:10	0.77	0.72	0.05	0.01	0.23	0.05	0.43	0.48	0.06
3/20/2014 5:10	0.72	0.71	0.22	0.01	0.14	0.01	0.34	0.35	0.23

Time	TN	DN	NO_3^-	NO_2^-	NH_4^+	PON	DON	TON	N_{ox}
	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
3/25/2014 17:00	0.66	0.56	0.12	0.02	0.17	0.10	0.25	0.35	0.13
3/26/2014 12:00	0.72	0.57	0.12	0.01	0.19	0.15	0.25	0.39	0.13
3/27/2014 13:00	0.52	0.50	0.05	0.01	0.30	0.02	0.13	0.15	0.06
3/28/2014 15:00	0.60	0.52	0.05	0.02	0.28	0.08	0.18	0.26	0.07
3/29/2014 9:00	0.71	0.60	0.16	0.02	0.15	0.12	0.27	0.38	0.18
3/29/2014 21:00	0.77	0.70	0.11	0.02	0.18	0.07	0.39	0.45	0.14
3/30/2014 9:00	0.73	0.73	0.06	0.02	0.24	0.00	0.40	0.40	0.08
3/30/2014 21:00	0.69	0.59	0.12	0.02	0.13	0.10	0.33	0.43	0.14
4/1/2014 16:30	0.69	0.60	0.08	0.02	0.09	0.08	0.42	0.50	0.10
4/2/2014 12:30	0.63	0.48	0.11	0.01	0.07	0.15	0.28	0.43	0.13
4/3/2014 15:00	0.57	0.49	0.19	0.01	0.12	0.08	0.15	0.24	0.21
4/4/2014 9:00	0.51	0.49	0.15	0.01	0.11	0.02	0.22	0.24	0.16
4/5/2014 9:00	0.52	0.43	0.16	0.01	0.07	0.09	0.18	0.28	0.17
4/6/2014 8:00	0.51	0.47	0.14	0.01	0.11	0.04	0.21	0.25	0.15
4/7/2014 16:10	0.45	0.43	0.05	0.01	0.21	0.02	0.16	0.18	0.06
4/8/2014 4:10	0.46	0.32	0.05	0.04	0.08	0.14	0.15	0.30	0.09
4/8/2014 16:10	0.32	0.23	0.05	0.01	0.05	0.09	0.13	0.22	0.06
4/9/2014 10:00	0.34	0.19	0.05	0.01	0.05	0.15	0.08	0.24	0.06
4/10/2014 8:50	0.38	0.24	0.05	0.01	0.05	0.14	0.13	0.27	0.06
4/11/2014 8:10	0.37	0.29	0.05	0.01	0.05	0.08	0.18	0.26	0.06
4/12/2014 8:10	0.33	0.24	0.05	0.01	0.05	0.09	0.13	0.22	0.06
4/13/2014 8:10	0.53	0.23	0.05	0.01	0.05	0.31	0.12	0.43	0.06

Time	TN	DN	NO_3^-	NO_2^-	NH_4^+	PON	DON	TON	N_{ox}
	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
4/14/2014 10:00	0.45	0.19	0.05	0.01	0.05	0.26	0.09	0.34	0.06
4/14/2014 22:00	0.46	0.35	0.05	0.01	0.05	0.11	0.24	0.36	0.06
4/15/2014 4:00	0.29	0.10	0.05	0.01	0.05	0.19	0.00	0.19	0.06
4/15/2014 10:00	0.37	0.18	0.05	0.01	0.05	0.18	0.08	0.26	0.06
4/15/2014 22:00	0.39	0.21	0.14	0.01	0.05	0.18	0.01	0.19	0.14
4/16/2014 10:00	0.41	0.24	0.10	0.01	0.08	0.18	0.05	0.23	0.10
4/17/2014 15:00	0.46	0.29	0.05	0.03	0.05	0.17	0.16	0.33	0.08
4/18/2014 11:00	0.39	0.21	0.05	0.01	0.09	0.18	0.06	0.24	0.06
4/19/2014 11:00	0.42	0.25	0.05	0.01	0.05	0.18	0.14	0.32	0.06
4/20/2014 11:00	0.41	0.23	0.05	0.01	0.05	0.18	0.12	0.30	0.06
4/21/2014 11:00	0.36	0.18	0.05	0.01	0.05	0.18	0.07	0.26	0.06
4/22/2014 11:00	0.43	0.25	0.05	0.01	0.05	0.18	0.15	0.33	0.06
4/23/2014 11:00	0.30	0.25	0.05	0.01	0.05	0.05	0.15	0.20	0.06
4/25/2014 16:40	0.47	0.37	0.05	0.01	0.05	0.10	0.26	0.36	0.06
4/26/2014 16:40	0.37	0.29	0.05	0.01	0.05	0.08	0.18	0.26	0.06
4/27/2014 16:40	0.38	0.37	0.05	0.01	0.05	0.01	0.26	0.27	0.06
4/28/2014 16:40	0.43	0.40	0.05	0.01	0.05	0.03	0.29	0.32	0.06
5/1/2014 14:20	0.55	0.41	0.15	0.01	0.05	0.14	0.20	0.34	0.16
5/2/2014 14:20	0.49	0.40	0.14	0.01	0.05	0.09	0.20	0.29	0.15
5/3/2014 14:20	0.51	0.38	0.10	0.01	0.05	0.13	0.22	0.35	0.10
5/4/2014 14:20	0.45	0.29	0.05	0.01	0.05	0.16	0.18	0.35	0.06
5/5/2014 14:20	0.47	0.31	0.05	0.01	0.05	0.16	0.20	0.36	0.06
5/6/2014 9:30	0.43	0.35	0.05	0.01	0.05	0.08	0.24	0.32	0.06

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